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Feasibility of Producing Elemental Sulfur from Magnesium Sulfite

Radian Corp, Austin, Tex

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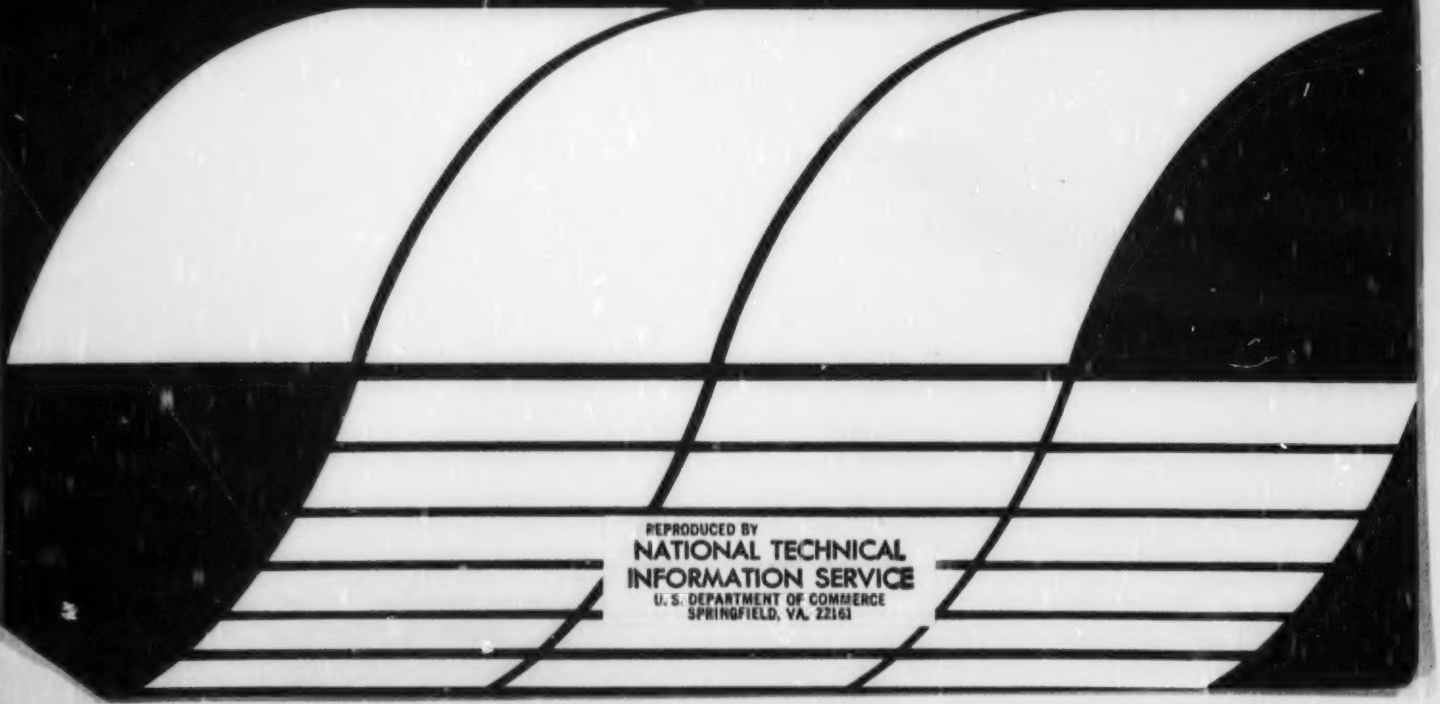
Energy-Environment
Research and Development
Program Report



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ABSTRACT

A study was made to extend the potential applications of MgO flue gas desulfurization processes by allowing the sulfur to be recovered as elemental sulfur as well as sulfuric acid. The particular question addressed in this study was the feasibility of combining the exothermic SO_2 reduction reaction with the endothermic $MgSO_3$ calcination.

Preliminary consideration of the reductants carbon monoxide, hydrogen, methane and hydrogen sulfide showed that the reaction with SO_2 can supply part, or in some cases all, of the heat of decomposition of $MgSO_3$. Two cases were considered in detail: (1) A low temperature catalytic decomposition using a commercially available low Btu syngas reductant mixture and (2) A high temperature noncatalytic decomposition using a medium Btu reducing gas from an oxygen-blown gasifier.

Complete heat and material balances for conceptual process designs for the above cases were made, in order to identify problem areas. Recommendations for work required to continue development of the process are given. Problem areas identified include catalyst physical stability, catalyst/MgO separation, dust carry-over, and noncatalytic SO_2 reduction kinetics.

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1.0 INTRODUCTION

The magnesium oxide (Mag-Ox) scrubbing process is a regenerable flue gas desulfurization technique which has been demonstrated on two major commercial-scale test facilities in this country. The chemical basis of this process is the reaction of SO_2 with MgO to form $MgSO_3$. The $MgSO_3$ crystals are calcined to regenerate MgO.[1] This produces an SO_2-rich gas stream which is used as feed to a sulfuric acid plant. That H_2SO_4 production is the only available process option for treating the SO_2 rich gas produced by $MgSO_3$ calcination limits the potential for future application of the MgO process.

An option other than H_2SO_4 production for the SO_2 is its reduction to elemental sulfur. Commercial technology is already available for this reduction, as will be discussed later. Combined with the commercially demonstrated $MgSO_3$ calcination, there results a complete regenerable flue gas desulfurization process. The question addressed in this report is the feasibility of combining the endothermic calcination with the exothermic SO_2 reduction. This combination does not appear to have been considered, but should result in considerable simplification of process heat transfer and better overall thermal efficiency. The objective of this study was to make an assessment of the technical feasibility of this combination option by means of a conceptual process design.

The study begins with a description of the state of the art of Mag-Ox and other pertinent technology. Next, a literature survey is presented that outlines what is known about $MgSO_3$ decomposition and SO_2 reduction to elemental sulfur. Preliminary calculations for the $MgSO_3$-reducing gas system are then made to identify promising temperature, reducing gas, and stoichiometry conditions. Based upon these preliminary calculations it was shown that (1) a reducing calciner that would use the heat given off by the exothermic SO_2 reduction reaction to provide the heat required by the endothermic $MgSO_3$ calcination reaction was feasible and (2) further treatment of the reducing calciner off gases was required for more complete conversion to elemental sulfur.

Process designs were calculated for two schemes. The first scheme requires a catalyst in the reducing calciner to promote the gas phase SO_2 reduction reaction. The calciner would operate at 500°C. The second scheme would not require a catalyst but would operate at 900°C. Both schemes require a low temperature catalytic process (similar to a Claus plant) for efficient conversion of the gaseous mixture to elemental sulfur.

The most significant process problems identified are the dusting of the $MgSO_3$ and its reaction products (with attendant effects on catalysts) and separation of catalyst from MgO in a catalytic reducing calciner. Information gaps are associated primarily with the reducing calciner. They include decomposition kinetics of $MgSO_3$ and SO_2 reduction in the $MgSO_3$-MgO system. Process development recognizing the above problems is recommended.

1.1 State-of-the-Art

1.1.1 Mag-Ox Process

Commercial scale experience with the magnesium oxide scrubbing process has been gained in the following two facilities.

- A prototype demonstration unit on a 155 Mw oil-fired boiler at Boston Edison's Mystic Station (tested from April 1972 to June 1974).
- A prototype demonstration unit on a 100 Mw coal-fired boiler at Potomac Electric Power's Dickerson Station (tested from September 1973 to September 1975).

Additional Mag-Ox scrubbing units which are either currently under construction or in advanced planning stages include:

- A 120 Mw installation at Philadelphia Electric's Eddystone Station (coal-fired) undergoing start-up.
- Planned expansions by Philadelphia Electric at their Eddystone (576 Mw of additional scrubbing capacity) and Cromley (150 Mw) stations.

Since the Boston Edison facility is representative of this process technology, the Mystic scrubbing system is used here as a basis for discussing important operating characteristics of magnesium oxide scrubbing systems in general. A schematic view of the Boston Edison MgO scrubbing system is shown in Figure 1-1.

In the Mag-Ox scrubbing process SO_2 sorption is accomplished by contacting hot flue gas with an aqueous alkaline solution of $MgSO_3$. Although a venturi scrubber was used in the Boston Edison system, this process can be used with any properly designed vapor/liquid contacting device. Key chemical reactions which take place in the Mag-Ox scrubbing system are the following:

- MgO hydration/dissolution

$$MgO(s) + H_2O(aq) \rightarrow Mg(OH)_2(s) \rightarrow Mg^{++}(aq) + 2OH^-(aq) \quad (1\text{-}1)$$

- SO_2 sorption

$$SO_2(g) \rightarrow SO_2(aq) \quad (1\text{-}2)$$

- SO_2 reaction

$$SO_2(aq) + 2OH^-(aq) \rightarrow SO_3^=(aq) + H_2O(aq) \quad (1\text{-}3)$$

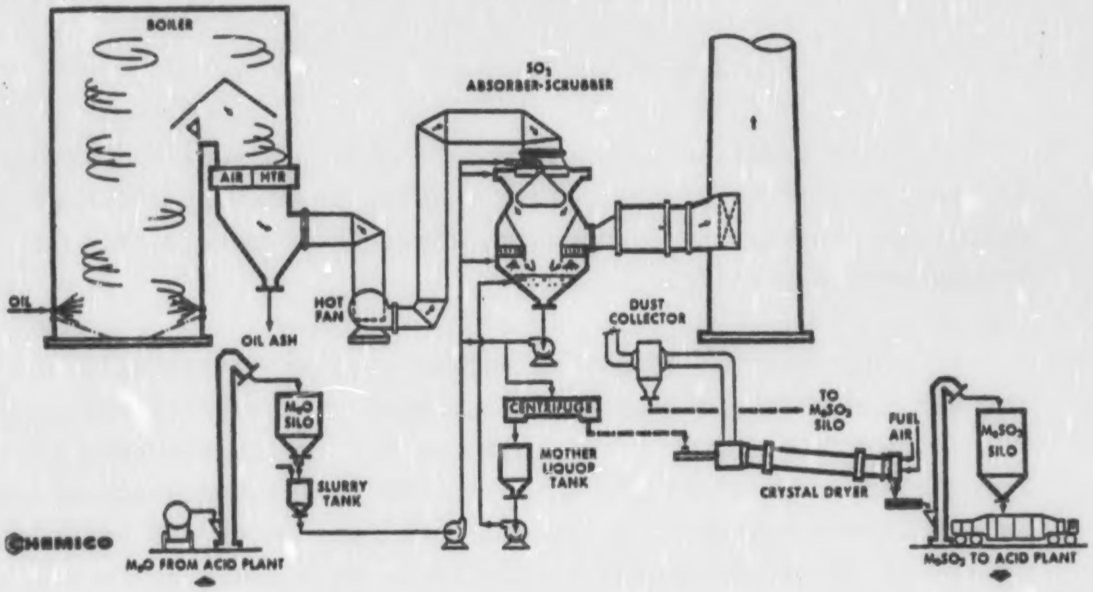
BOILER
SO_2 ABSORBER-SCRUBBER
AIR HTR
OIL
OIL ASH
HOT FAN
DUST COLLECTOR
CENTRIFUGE
TO $MgSO_3$ SILO
FUEL AIR
MOTHER LIQUOR TANK
MgO SILO
SLURRY TANK
CRYSTAL DRYER
$MgSO_3$ SILO
CHEMICO
MgO FROM ACID PLANT
$MgSO_3$ TO ACID PLANT

FIGURE 1-1. PROCESS FLOW SHEET FOR BOSTON EDISON MgO-SO_2 SCRUBBING SYSTEM (OIL-FIRED BOILER)

Source: (KO-134)

. sulfite precipitation

$$Mg^{++}(ag) + SO_3^{=}(aq) + xH_2O(aq)$$

$$\rightarrow MgSO_3.xH_2O(s) \qquad (1\text{-}4)$$

$x = 3$ or 6.

In addition to these main reactions, some oxidation of product sulfite occurs. This results in the formation of $MgSO_4$, an undesirable by-product, since it is more difficult to regenerate than $MgSO_3$.

Net removal of sorbed sulfur species is accomplished through the precipitation and continuous discharge of $MgSO_3$ solids from the system. $MgSO_4$ is removed in the adherent water. Product $MgSO_3$ crystals are dried at 200°C, a temperature which is sufficiently high to drive off both free water and associated waters of hydration ($MgSO_3$ precipitates in a hydrated form $MgSO_3 \cdot xH\ O$; where "x" equals either 3 or 6 depending on the conditions of operation). At the same time, however, the exit temperature of the $MgSO_3$ solids leaving the drier must be kept below the value at which thermal decomposition of $MgSO_3$ begins to occur ($MgSO_3 \rightarrow MgO + SO_2$). One aspect of the $MgSO_3$ drying process which has a significant impact upon downstream processing requirements is related to the dehydration step. As the $MgSO_3$ solids lose their waters of hydration, the thermal and mechanical stresses which accompany this reaction tend to result in the formation of product solids which are very finely divided. This can create severe dust and reagent loss control problems. This aspect of the regeneration problem is discussed in some detail in a later section of this report.

The processing scheme which is currently being used to regenerate MgO is shown in Figure 1-2. In the case of the

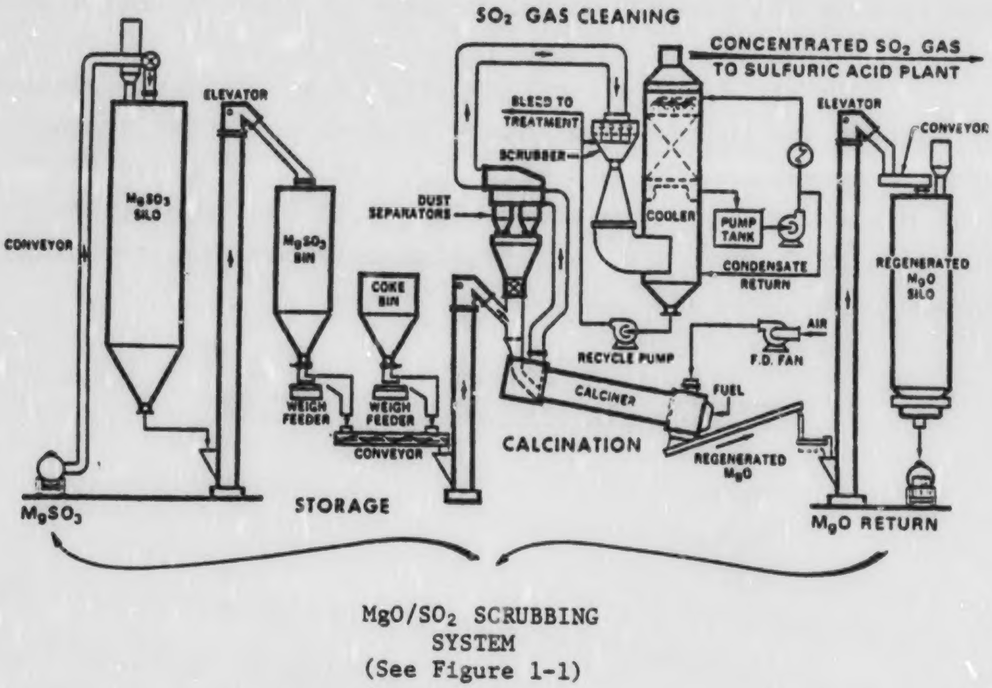
SO₂ GAS CLEANING
CONCENTRATED SO₂ GAS
TO SULFURIC ACID PLANT
ELEVATOR
BLEED TO TREATMENT
SCRUBBER
ELEVATOR
CONVEYOR
MgSO₃ SILO
CONVEYOR
DUST SEPARATORS
MgSO₃ BIN
COOLER
PUMP TANK
REGENERATED MgO SILO
CONDENSATE RETURN
COKE BIN
AIR
RECYCLE PUMP
F.D. FAN
FUEL
CALCINER
WEIGH FEEDER
WEIGH FEEDER
CONVEYOR
CALCINATION
REGENERATED MgO
STORAGE
MgSO₃
MgO RETURN
MgO/SO₂ SCRUBBING
SYSTEM
(See Figure 1-1)

FIGURE 1-2. PROCESS FLOW SHEET OF EXISTING $MgSO_3$ REGENERATION FACILITY

Source: (KO-134)

Boston Edison System and in the final phases of the Potomac Electric Power program, MgO was regenerated in a facility operated by the Essex Chemical Company in Rumford, Rhode Island.

In the Essex plant, $MgSO_3/MgSO_4$ solids were calcined by heating the solids in a rotary kiln at essentially atmospheric pressure. The mid-kiln temperature was about 680°C. Coke was added to the calciner along with the feed solids to act as a $MgSO_4$ reductant. A typical calciner feed composition is shown in Table 1-1 (EN-316).

TABLE 1-1

TYPICAL CALCINER FEED COMPOSITION

$MgSO_3$	63.9
$MgSO_4$	12.7
MgO	2.8
Water and Inerts	21.0

The principal reactions which take place in the calciner are:

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (1\text{-}5)$$

$$MgSO_4 + \tfrac{1}{2}C \rightarrow MgO + SO_2 + \tfrac{1}{2}CO_2 \qquad (1\text{-}6)$$

The existing process yields a solid product which is 98% MgO. The gas stream leaving the calciner is a dilute SO_2 mixture whose approximate composition is given in Table 1-2.

TABLE 1-2

TYPICAL CALCINER EXIT GAS COMPOSITION

N_2	73
CO_2	6
O_2	5
H_2O	7
SO_2	9

The residence time of the solid phase in the calciner is about one hour (ZO-008).

In spite of some operational difficulties which have been experienced with the $MgSO_3$ calcination process described above, this technology has been shown to be a viable regeneration process option. Likewise, the production of sulfuric acid from SO_2 is proven technology.

The direct reduction of $MgSO_3$ to produce MgO and elemental sulfur does not appear to have been attempted on a commercial scale. Available information on related process technology, however, indicates that one approach to $MgSO_3$ regeneration which does appear to be feasible is a two-step process involving the decomposition of $MgSO_3$ to MgO and SO_2 followed by a gas phase SO_2 reduction step. For this reason, it is appropriate here to discuss the status of existing technology for producing elemental sulfur from SO_2.

1.1.2 Elemental Sulfur Production from SO_2

Three elemental sulfur production techniques which have particular relevance to the present study are the following:

- Allied Chemical Process,
- Asarco-Phelps Dodge Process,
- Outokumpu Oy Process.

General operating characteristics of each of these processes are summarized in Table 1-3.

It is obvious from the information presented in the table that all existing processes for producing elemental sulfur from SO_2 are similar with respect to their general principle of operation. In each case, SO_2 is reacted with an appropriate reducing gas such as CH_4, CO, H_2 (or a mixture thereof) to form elemental sulfur, COS, and H_2S. Since equilibrium sulfur production is maximized at low temperatures, there appears to be an incentive for using a catalyst to promote this initial reducing gas/SO_2 reaction since this option provides favorable kinetics at lower temperatures. SO_2 conversion is controlled so that an $H_2S:SO_2$ mole ratio of 2:1 is obtained in the product gas. With this approach, a tail end Claus reactor can be used to convert residual SO_2 and H_2S to additional elemental sulfur ($2H_2S + SO_2 \rightarrow 3S + 2H_2O$). A more detailed discussion of these sulfur production technologies is presented in Technical Note 200-045-31-01a in the Appendix of this report.

1.2 Subtask Description

In this section, a general description is presented of the technical approach which was followed in assessing the feasibility of producing MgO and elemental sulfur from $MgSO_3$. Basically, overall effort on this program was divided into the five major subtask areas shown in Figure 1-3. A general description of the work performed during each of these

TABLE 1-3

COMMERCIAL PROCESSES FOR PRODUCING SULFUR FROM SO_2

Process Developer and Location	Application	Feed Properties	Process Details*
Allied Chemical - Sudbury, Ontario, Canada	Treatment of tail gas from sulfide ore roasting facility.	Gas: 12% SO_2	Catalytic reduction of SO_2 with methane Key reactions are: $CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + S_2$ $4CH_4 + 6SO_2 \rightarrow 4CO_2 + 4H_2O + 4H_2S + S_2$ Optimum reaction conditions are those which yield: (1) maximum conversion of SO_2 to elemental sulfur (over 40%) (2) a product gas containing H_2S and SO_2 in a 2:1 mole ratio. After the product sulfur is condensed, a two-stage Claus reactor system is used to convert the remaining H_2S and SO_2 to sulfur and water. $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ 90+% conversion efficiency has been demonstrated.
Asarco-Phelps Dodge - El Paso, Texas	Pilot plant for treatment of Cu-Pb smelter tail gas.	Gas: 10-15% SO_2 2-3% O_2	Catalytic reduction of SO_2 with CO/H_2 mixture produced by methane reforming. 70% conversion of SO_2 to S achieved in primary reactor. Residual H_2S/SO_2 reacted in single stage Claus reactor. Total sulfur recovery obtained: 88-92%.
Outokumpu Oy Company - Finland	Production of FeO, elemental sulfur and sulfuric acid from pyrite ore (FeS_2).	FeS_2 Solids	Solids are suspended in hot reducing gas produced by partial oxidation of fuel oil in a flash smelter. CO and H_2 react with SO_2 to produce S and H_2S as the gases are cooled (non-catalytic). Reaction of H_2S and SO_2 to produce more sulfur occurs as the gases are cooled further. Sulfur yield is optimized by passing residual H_2S and SO_2 over an alumina catalyst at 270°C.

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* More complete descriptions of these processes are presented in the Appendix to this report in Technical Note 200-045-31-01.

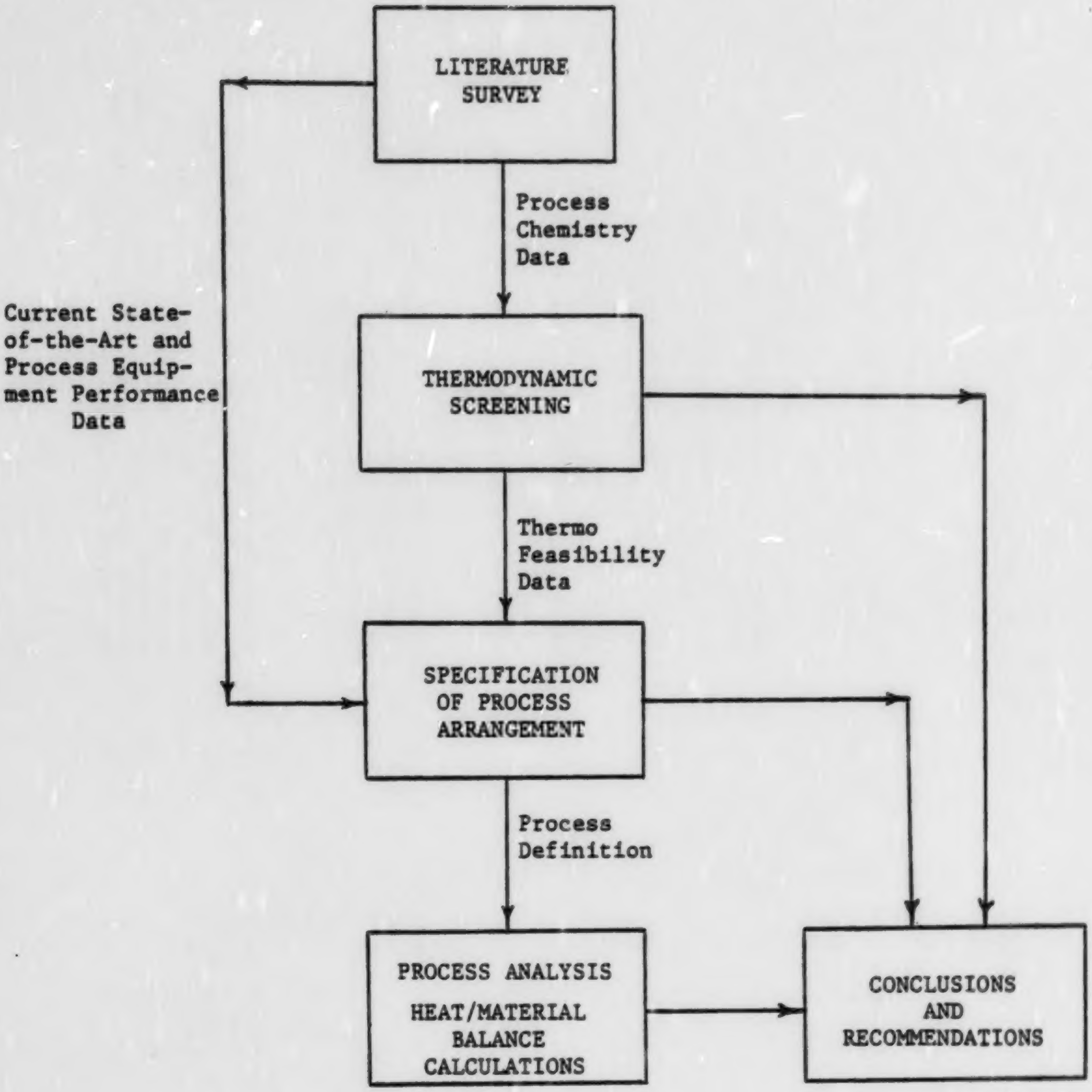

LITERATURE SURVEY
Process Chemistry Data
Current State-of-the-Art and Process Equipment Performance Data
THERMODYNAMIC SCREENING
Thermo Feasibility Data
SPECIFICATION OF PROCESS ARRANGEMENT
Process Definition
PROCESS ANALYSIS
HEAT/MATERIAL BALANCE CALCULATIONS
CONCLUSIONS AND RECOMMENDATIONS

FIGURE 1-3. SUBTASK BREAKDOWN FOR STUDY TO DEFINE THE FEASIBILITY OF PRODUCING ELEMENTAL SULFUR FROM $MgSO_3$

subtasks is presented below.

Subtask 1 - Literature Survey

The goal of this subtask was the collection and analysis of three different types of data:

- Chemistry of the Mg-O-S System

  These data were needed to define potential methods of producing elemental sulfur from $MgSO_3$.

- Relevant Process Technology

  This portion of the literature survey provided background data for the state-of-the-art discussion presented in Section 1.1. Equipment performance data were also gathered as part of this subtask for use in subsequent phases of the program.

- Kinetic Data

  Two types of kinetic data were sought: (1) $MgSO_3$ solids decomposition reactions; (2) sulfur forming reactions involving such gas phase components as CH_4, CO, H_2, H_2O, H_2S, COS and SO_2. These data were needed to define conditions under which the reactions of interest would proceed at favorable rates.

Subtask 2 - Thermodynamic Screening

Equilibrium calculations for promising reaction systems were performed to determine the influence of temperature and stoichiometry on gaseous and solid phase product distributions.

Subtask 3 - Possible Process Arrangements

Using information from the literature and guided by the results of Subtask 2 above, conceptual processing strategies utilizing various types of equipment and process arrangements were developed. Factors considered here include the temperature ranges of interest, energy transfer considerations, process simplicity, and so on. One low temperature process using a low Btu gas was investigated. The low temperature will involve a gas phase catalyst so that the endothermic decomposition heat can be supplied by the exothermic gas phase reduction reaction. Three noncatalytic high temperature decompositions were investigated. Reductants were a low Btu gas (air blown gasifier), a medium Btu gas (oxygen blown gasifier), and H_2S.

Subtask 4 - Heat and Material Balances

Heat and material balance calculations were performed for the promising process arrangements and reductants of choice devised in Subtask 3. These calculations, which were intended to determine the performance characteristics and energy requirements of an integrated sulfur recovery system, were made by assuming that equilibrium was reached in all process reaction vessels.

Subtask 5 - Conclusions and Recommendations

Based upon the results of the above four subtasks, promising approaches to elemental sulfur production and gaps in the existing process data base were identified. Also, recommendations for future studies of this problem were proposed.

2.0 TECHNICAL BACKGROUND

In this section justification is presented for the selection of specific processing schemes for producing elemental sulfur from $MgSO_3$ which appear to be technically feasible. The information presented here is based mainly upon data collected in the literature survey subtask.

2.1 Process Chemistry

This section summarizes the pertinent results of the process chemistry portion of the literature survey subtask. A more complete description of the results of this effort is presented in Technical Note 200-045-31-01a which is in the Appendix of this report.

As a result of this subtask, it was concluded that a two-step approach to the production of elemental sulfur from $MgSO_3$ is required. No reports of a direct reaction between $MgSO_3$ solids and a reducing agent to form elemental sulfur were found. For this reason, effort on this subtask was directed toward defining (1) the chemistry of $MgSO_3$ decomposition and (2) general gas phase reactions of the form:

$$\begin{aligned} &SO_2 + \text{Reducing Gas} \\ &\quad \rightarrow \text{Elemental Sulfur} + \text{By-Product} \end{aligned} \tag{2-1}$$

The chemistry of $MgSO_3$ decomposition will be discussed first.

2.1.1 $MgSO_3$ Decomposition

Two hydrated forms of $MgSO_3$ exist: a tri- and a hexahydrate. Both can be formed in MgO flue gas desulfurization systems. Several investigators have studied the thermal behavior of $MgSO_3$ solids. Starting with the hexahydrate, three waters of hydration are lost as the solid is heated between 60 and 100°C. By 200°C the last three waters are lost. Some sulfite decomposition is also observed at this temperature.

$MgSO_3$ decomposition rates become significant at temperatures in the 300-600°C range. Decomposition of $MgSO_3$ in a nitrogen atmosphere at temperatures > 300°C yields measurable quantities of MgO, SO_2, $MgSO_4$, free sulfur and MgS_2O_3 (up to 550°C, magnesium thiosulfate is unstable at higher temperatures). Experimental evidence suggests that the above products are formed according to the following reactions:

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (2\text{-}2)$$

$$2MgSO_3 + SO_2 \rightarrow 2MgSO_4 + \tfrac{1}{2}S_2 \qquad (2\text{-}3)$$

$$MgSO_3 + \tfrac{1}{2}S_2 \rightarrow MgS_2O_3 \qquad (2\text{-}4)$$

$MgSO_3$ decomposed very rapidly at temperatures > 600°C. An empirical expression for the decomposition rate of $MgSO_3$ developed by Kim (KI-110) indicates reaction times of 38 seconds for 90% decomposition at 700°C and 30 seconds for 99% decomposition at 800°C.

2.1.2 Chemistry of Reduction of SO_2 to Elemental Sulfur

In this portion of the literature survey thermodynamic, kinetic, and other pertinent information pertaining to the chemistry of obtaining elemental sulfur from sulfur dioxide was reviewed. The literature was searched from 1967 through the present using Chemical Abstracts. Previous literature reviews were relied on for access to key investigations conducted prior to 1967.

Reducing agents which were considered include:

- methane,
- carbon monoxide,
- hydrogen,
- $CO + H_2$
- carbon,
- coal,
- H_2S.

Each of these systems is discussed in detail in Technical Note 200-045-31-01a in the Appendix. Important characteristics of these systems which are pertinent to the overall scope of this study are discussed in summary fashion below.

2.1.2.1 SO_2 Reduction by Methane

The use of methane as a reducing agent for sulfur dioxide has been developed for commercial use by Allied Chemical Corporation. A number of investigations have also been carried out by several groups of Soviet scientists.

The overall reaction of interest in this system is:

$$2SO_2 + CH_4 \rightarrow S_2 + CO_2 + 2H_2O \qquad (2\text{-}5)$$

Side reactions which result in the formation of H_2S, COS, and CS_2 are also significant.

In kinetic studies of this system, maximum elemental sulfur yields were obtained at $SO_2:CH_4$ ratios of 2:1 and at high temperatures. Bauxite was shown to be an effective catalyst at $T > 800°C$. In a non-catalytic system, this reaction is slow for $T < 1200°C$.

2.1.2.2 Reduction of Sulfur Dioxide by Carbon Monoxide

The reduction of SO_2 by carbon monoxide has been the subject of numerous investigations. The main reaction of interest here is

$$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2 \qquad (2\text{-}6)$$

In the absence of a catalyst this reaction is slow for $T < 1000°C$; therefore the emphasis of many studies of SO_2 reduction by CO is on catalysis. The performance characteristics of a wide range of alumina based catalysts have been studied experimentally. Catalytic systems show favorable rates and first order kinetics at temperatures greater than 400°C. COS formation is a major problem.

2.1.2.3 Reduction of Sulfur Dioxide with Hydrogen

The main reaction of interest here is

$$SO_2 + 2H_2 \rightleftarrows 2H_2O_{(g)} + \frac{1}{2}S_2 \qquad (2\text{-}7)$$

however, H_2S formation reactions are also significant in this system. Thermodynamically, the formation of elemental sulfur is favored by low temperatures ($T < 400°C$), however, the uncatalized reaction proceeds too slowly at those temperatures to be feasible from a commercial standpoint. With an appropriate (bauxite or reduced alunite) catalyst, favorable kinetics were obtained once temperatures in the 300-500°C range were reached. The uncatalyzed reaction apparently proceeds slowly at temperatures below 900°C.

2.1.2.4 Reduction of Sulfur Dioxide with CO + H_2

A number of studies of SO_2 reduction by converted natural gas are reported in the literature. Both catalytic and non-catalytic systems have been studied. Although this system has not been studied as extensively as those discussed previously, its behavior follows the same patterns which were discussed for the pure component cases.

2.1.2.5 Sulfur Dioxide Reduction by Coal

One reference to the reduction of SO_2 with coal was found in the recent literature - a patented gas purification process involving the reaction of an SO_2-rich gas with coal at temperatures $\geq$ 425°C (ST-322). A high sulfur content coal may be used. No additional information was available in the abstract of this patent.

2.1.2.6 Sulfur Dioxide Reduction by Carbon

Studies of the reduction of SO_2 by various forms of carbon have been reported in the literature. Mechanisms have been suggested involving formation of carbon-sulfur and carbon-oxygen bonds. Lepsoe (LE-175) reported that in the presence of carbon, continuous reduction of SO_2 takes place through the following reaction scheme:

$$SO_2 + C = CO_2 + \tfrac{1}{2}S_2 \qquad (2\text{-}8)$$

$$CO_2 + C = 2CO \qquad (2\text{-}9)$$

$$2CO + SO_2 = 2CO_2 + \tfrac{1}{2}S_2 \qquad (2\text{-}10)$$

Above 650°C, these reactions proceed very rapidly. CS_2 and COS formation can occur with this system.

2.1.2.7 Sulfur Dioxide Reduction by H_2S

This reaction is discussed below. Equilibrium distribution will be similar to reduction of SO_2 with H_2S. The kinetics are similar to the Claus reaction.

2.1.3 Other Potentially Important Reactions

Many of the reactions between reducing gases and SO_2 produce significant quantities of undesirable by-products. CO for example reacts with SO_2 to produce not only elemental sulfur but also COS and CS_2. Hydrogen (or H_2O) containing reducing gases can react to form H_2S.

Because some of these side reactions progress to a significant extent under conditions which are favorable for the production of elemental sulfur from SO_2, possible mechanisms for the conversion of these by-product species to elemental sulfur were considered. A summary of the results of this portion of the literature survey subtask is presented below.

2.1.3.1 Conversion of H_2S to Elemental Sulfur

The majority of the processes which are available to accomplish this conversion step are based upon the Claus reaction.

$$SO_2 + 2H_2S \rightarrow 2H_2O + \frac{3}{x} S_x$$

A large number of commercially proven process variations based upon this reaction system are available. These are discussed in detail in the Appendix (see Technical Note 200-045-31-01a).

2.1.3.2 COS/CS_2 Formation

COS and CS_2 formation occur as a result of gas phase reactions between CO_2, CO, SO_2, and elemental sulfur. This problem area is best avoided by choosing reaction conditions (temperature, catalyst, reducing gas, composition, and stoichiometry) which minimize the yields of these species. The use of a reducing gas containing H_2 also minimizes this problem.

2.2 Thermodynamic Screening

The objective of the thermodynamic screening subtask was to examine the equilibrium sulfur yields which could be obtained through the reaction of $MgSO_3$ with various reducing gases. Equilibrium calculations were performed to determine the influence of temperature, gas phase composition, and stoichiometry on the gaseous and solid phase product distributions which would be obtained if $MgSO_3$ were calcined in the presence of a reducing gas. Overall heat balances for each reaction system were also calculated.

2.2.1 Selection of Cases

Calculations were made for four reducing gases at five stoichiometries and four temperatures (a total of 80 cases). Reducing gases of CO, H_2, CO + H_2, and CH_4 were selected on the basis of their availability and their demonstrated capability for reducing SO_2 to elemental sulfur. H_2S will be similar to H_2 as far as equilibrium product distribution is concerned. The stoichiometries of these reducing agents were varied both to find the optimum conditions for elemental sulfur production and to simulate ranges of conditions that would be found in fluidized bed, co-current, or counter current reactors. A complete discussion of the gas-solid flow conditions and temperature profiles obtained in each different type of reactor is included in the Appendix (Technical Note 200-045-31-02). The four temperatures of 350, 500, 700, and 1000°C were chosen to include the lower limit of 350°C for $MgSO_3$ decomposition and the upper limit of 1000°C for non-catalytic reduction of SO_2 to sulfur. Table 2-1 shows the selected equilibrium conditions.

TABLE 2-1
EQUILIBRIUM CASES

Four Temperatures (°C): 350; 500; 700; 1000.

Five Stoichiometries: 0.95; 1.0; 1.05; 1.5; 20.0.

Four Reducing Gases: 100% CH_4; 100% CO; 100% H_2;
CO/H_2 (50% each).

An energy balance around the overall process was made possible by specifying the inlet temperatures of the gas and solid streams involved in each case. A temperature of 25°C was chosen for the $MgSO_3$ solids and the CH_4 reducing gas. The other three reducing gases, H_2, CO, and the H_2/CO mixture, were specified to be at 1000°C for purposes of computing reaction system energy balances. H_2, CO, and H_2/CO were assumed to be hot since these gases would most likely be produced on site using some sort of reforming or gasification process.

The gas and solid species which were considered in these calculations are listed in Table 2-2. These species were selected on the basis of their potential for existence in the reactor as determined by the literature survey. For the majority of the species considered, thermodynamic properties were obtained from the well-known JANAF Thermochemical Tables (ST-067). Some data for MgS_2O_3 were estimated.

TABLE 2-2
CHEMICAL SPECIES CONSIDERED IN THERMODYNAMIC SCREENING

Gas		
H	CO	S
H_2	CO_2	S_2
H_2O	COS	S_8
H_2S	CS_2	SO_2
O_2	CH_4	SO_3
	MgS	

Condensed Phase	
MgO	$MgSO_3$
MgS	$MgSO_4$
S (liquid)	MgS_2O_3
C (graphite)	$MgCO_3$

It should be noted here that, in the interests of simplifying the computational procedures involved, S, S_2 and S_8 were the only gas phase sulfur species which were considered in the initial screening portion of the thermodynamic calculations which were performed as part of this subtask. In actual fact, gaseous elemental sulfur with three through seven atoms of sulfur per molecule can also exist at the conditions which were of interest here. The total amount of elemental sulfur vapor is still fairly well approximated by only S_2 and S_8. For this reason, ignoring the S_{3-7} components does not affect the results of these screening calculations. In subsequent process design calculations, all potentially significant gas phase species were included.

2.2.2 Results of Thermo Screening Calculations

The results of the equilibrium calculations for the 80 different reaction cases considered are shown in Tables B3-1 through B3-8 of Technical Note 200-045-31-02 in Appendix B. In all of the cases, the $MgSO_3$ was completely decomposed. The main decomposition product was MgO. Some $MgSO_4$ was formed in certain low-temperature, low-stoichiometry cases. In none of the cases were MgS_2O_3 or MgS thermodynamically stable.

When CO was used as a reducing gas close to a stoichiometric amount, virtually all of the solid product appeared as $MgCO_3$ at 350°C. This would not be a process problem area, however. Even if $MgCO_3$ were formed, it would decompose during the scrubbing process to MgO and CO_2. $MgCO_3$ formation would be an economic penalty because of shipping costs since it weighs almost twice as much as MgO.

The two reducing agents containing carbon (CH_4 and CO) showed large solid carbon formation tendencies at high stoichiometries. This indicates that coke formation at the gas inlet to a fluid bed or counter current calciner could be a potential problem area. Coke deposition could cause problems if the process is catalytic.

The highest sulfur yields occurred for the cases in which CO was used as a reducing gas. At a CO stoichiometry of 1.0 the elemental sulfur yield for this case was always above 80%. At $T < 450°C$ and $600°C < T < 800°C$, a 90+% equilibrium elemental sulfur yield is obtained. This is shown in Figure 2-1. With H_2, the equilibrium sulfur yield is considerably less than that obtained with CO as shown in Figure 2-2. The equilibrium sulfur yield for CH_4 is intermediate between those obtained with CO and H_2 as shown in Figure 2-3.

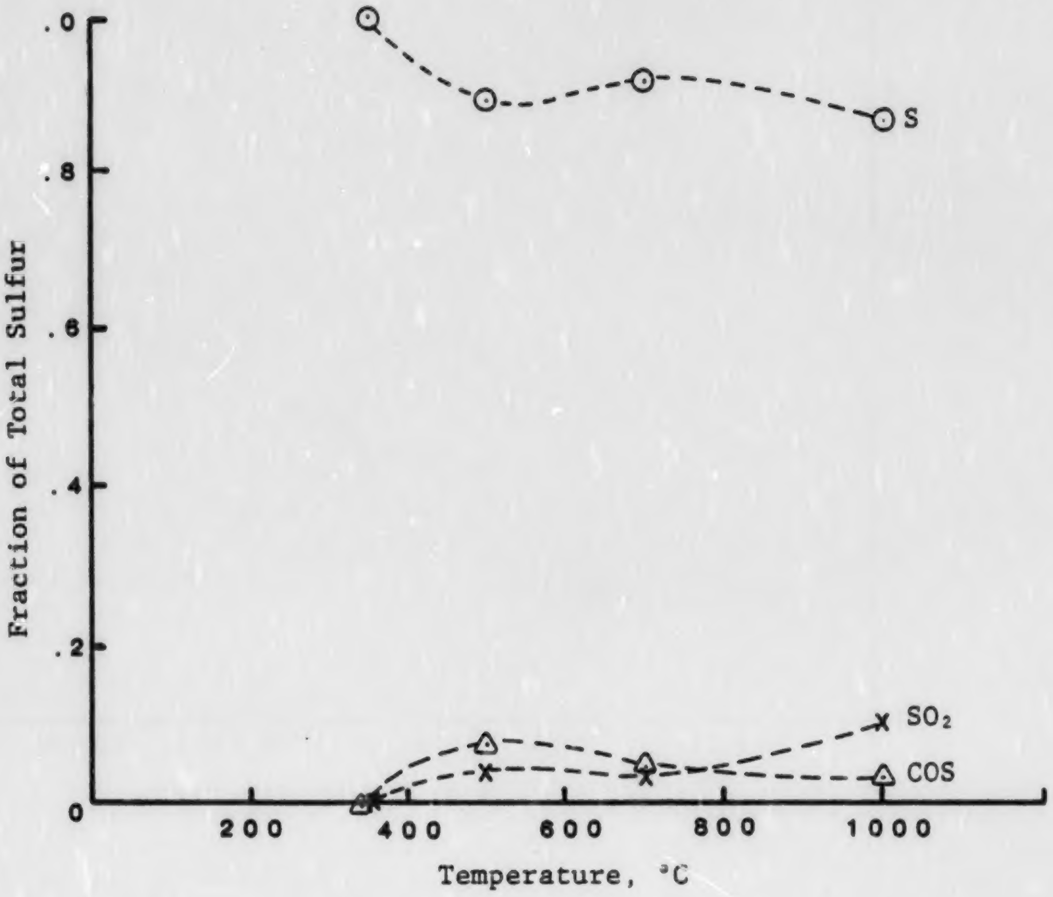


FIGURE 2-1. EQUILIBRIUM SULFUR DISTRIBUTION WITH CO

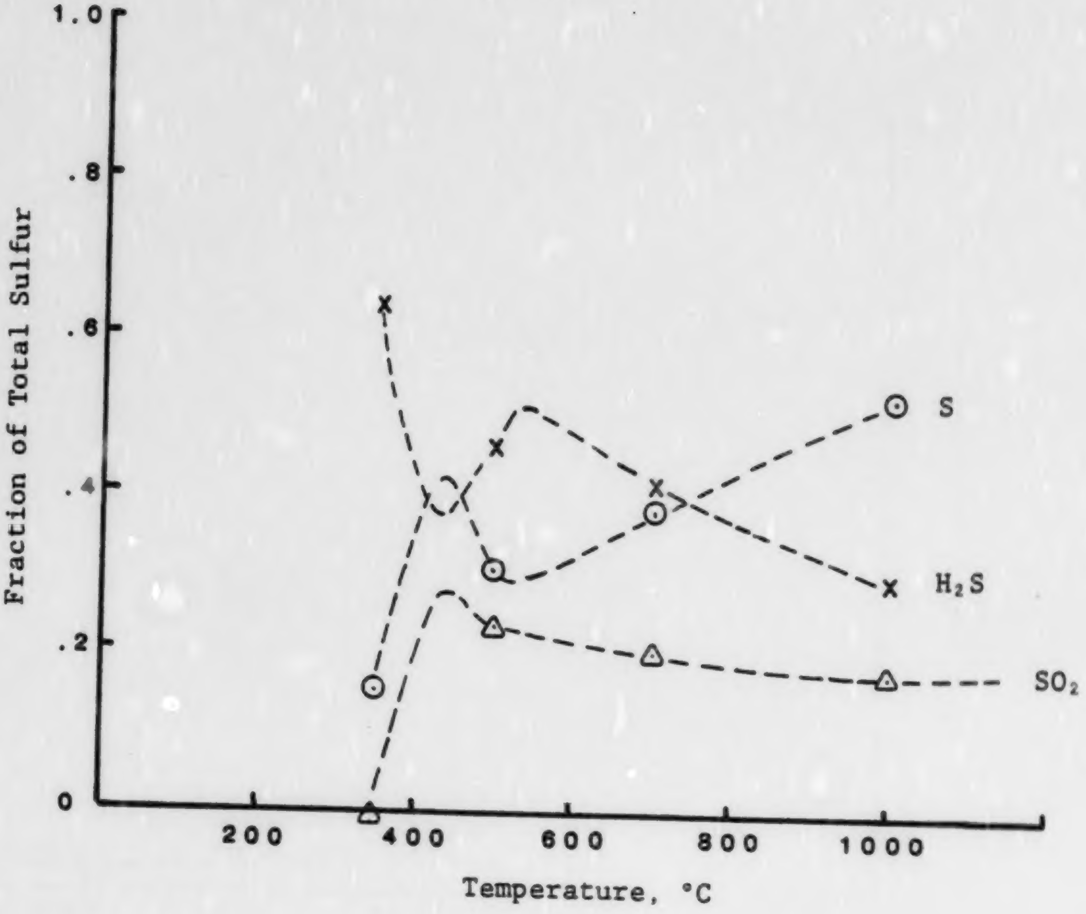


FIGURE 2-2. EQUILIBRIUM SULFUR DISTRIBUTION WITH H_2

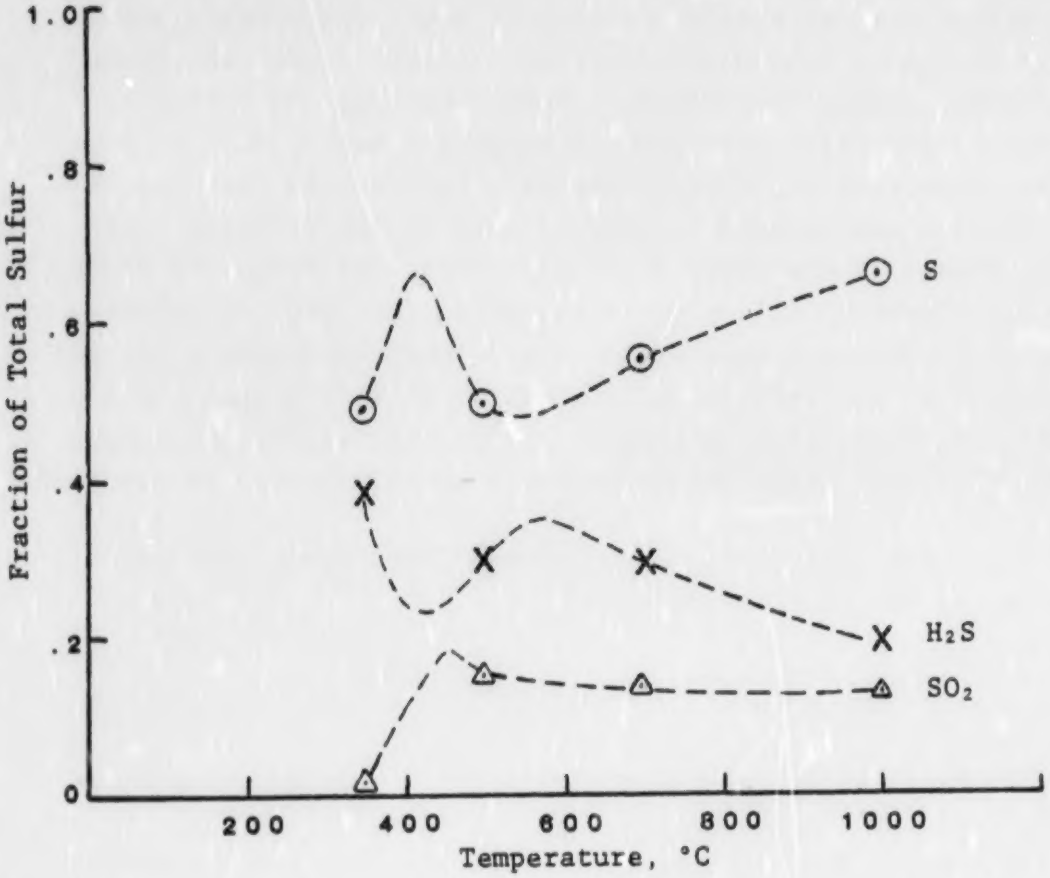


FIGURE 2-3. EQUILIBRIUM SULFUR DISTRIBUTION WITH CH_4

Since the initial screening at four widely-spaced temperatures indicated a number of apparent anomalies in the equilibrium products if plotted, a closer look was taken at H_2, H_2S, and H_2 + CO at a stoichiometry of one. The results are shown in Figure 2-4, where fraction of total elemental sulfur is plotted versus temperature. Both a maximum and minimum appear in all three cases, but are readily explainable in terms of the reactions and thermodynamics involved. In the initial low temperature region no $MgSO_3$ appears in the products, but $MgSO_4$ does. As the temperature increases, the $MgSO_4$ decreases, and the elemental sulfur increases until the $MgSO_4$ disappears. With no further increase of SO_2 due to $MgSO_4$ decomposition, the elemental sulfur declines with temperature in the range of 400-550°C. In this range, the major sulfur species are the larger ones, S_{6-8}, for which the formation from SO_2 and H_2S is exothermic.

The sulfur yield goes back up with temperature as more S_2 is formed. The reaction

$$2H_2S + SO_2 = 2H_2O + \frac{3}{x} S_x$$

is endothermic by 11.5 kcal at 298°K for x = 2, and exothermic by 26 kcal for x = 8. In the higher temperature region, the overall result for all S species is endothermic and the yield increases with increasing temperature. For the simple gaseous reaction, $SO_2 + 2H_2S$, there is no MgO in the reaction system. This eliminates the possibility of $MgSO_4$ formation and the usual plot of elemental sulfur formation versus temperature results as is shown in Figure 2-5.

A significant consideration is that the equilibrium conversion to elemental sulfur is a minimum in the 550-700°C range.

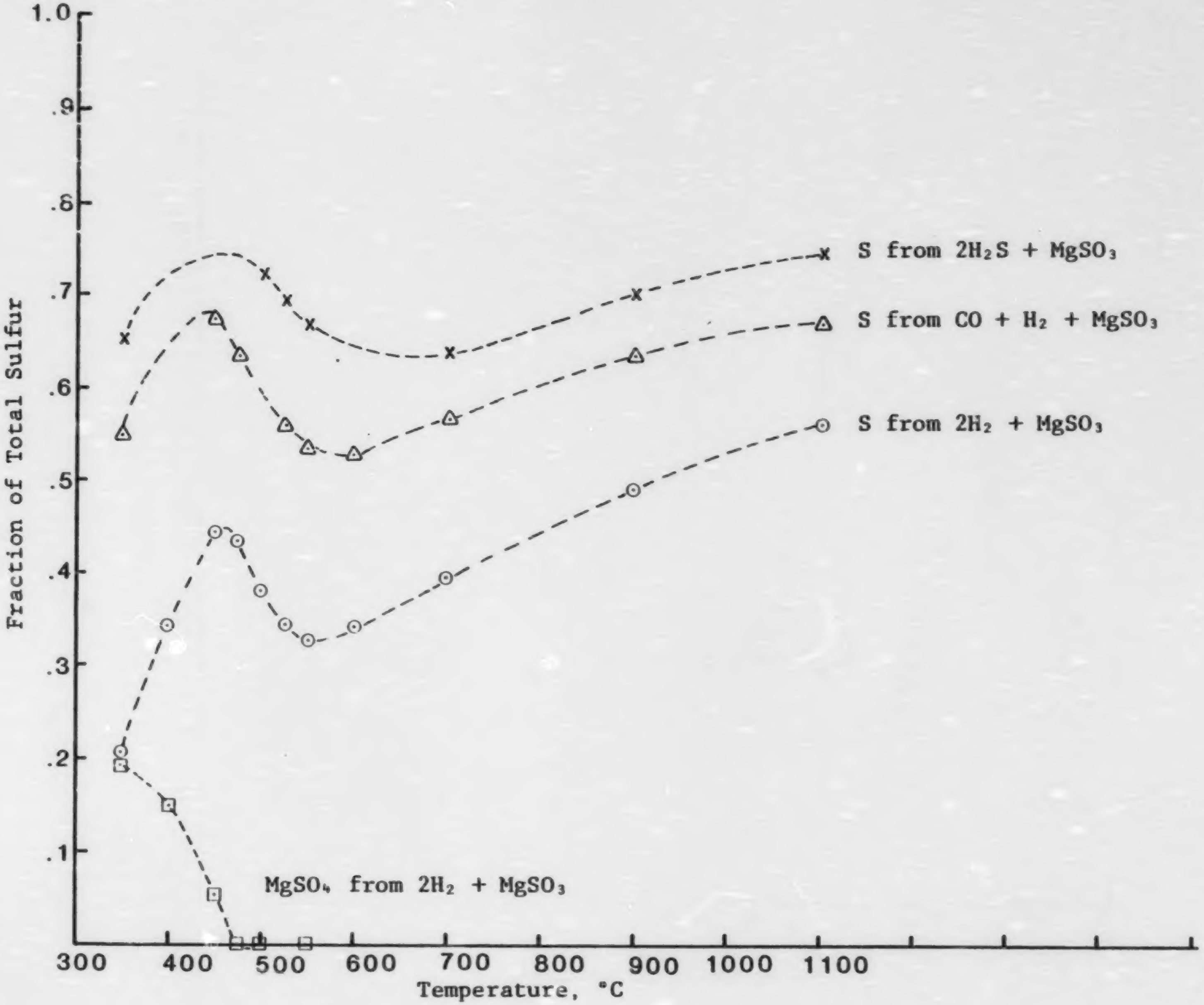


FIGURE 2-4. REDUCING GAS/$MgSO_3$ REACTION SYSTEM

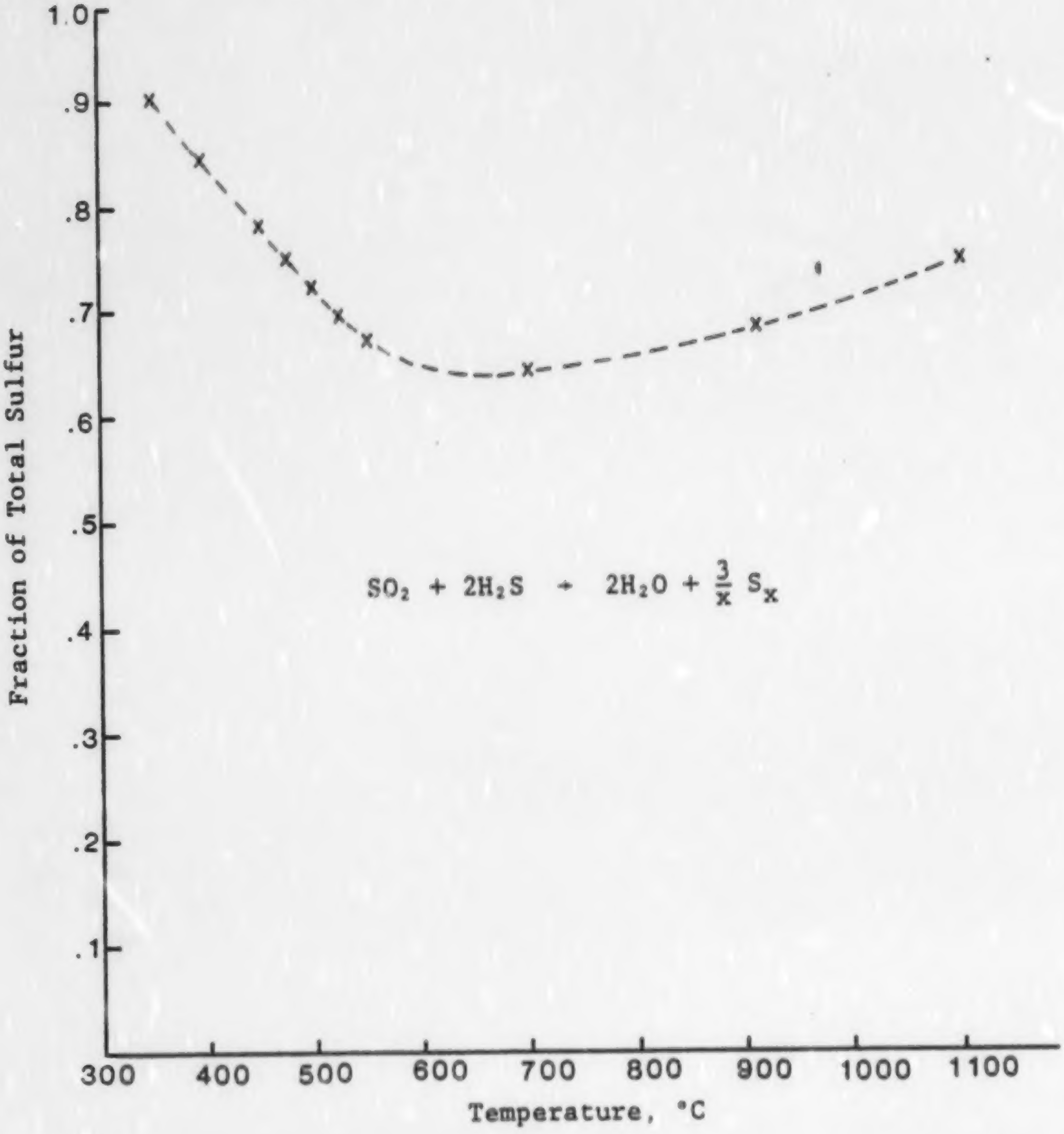


FIGURE 2-5. THE H_2S/SO_2 REACTION SYSTEM

In the cases where an excess of reducing gas was used, all of the excess H_2 tended to form H_2S and all of the excess CO to form COS. H_2S formation tendencies were greater than COS formation tendencies. Kinetic considerations would therefore provide the only incentive for operating the calcination reactor with an excess of reducing gas.

The heat balance numbers which were generated along with the equilibrium composition data are of interest because they indicate whether it is necessary to provide or remove heat from the reactor in order to maintain the specified steady state temperature. It is obviously desirable to minimize the need for transfer of heat. When using methane as a reducing agent, the reactor would require the addition of heat. The adiabatic operating temperature is between 700 and 1000°C for CO and between 500 and 700°C for H_2. Each reaction system is exothermic below these temperatures. The heat requirements for mixtures of H_2 and CO fall between those of the pure components.

2.3 Process Implications

Based upon the process chemistry and thermodynamic considerations discussed in previous sections, it is possible to identify a variety of factors which are pertinent to the conceptual design of a technically feasible sulfur-from-$MgSO_3$ process. Some of these factors are discussed in detail below.

Since the decomposition of $MgSO_3$ is endothermic and the reduction of SO_2 is exothermic in the lower temperature ranges, there is a large incentive for combining the calcination and SO_2 reduction steps in one reactor. The thermodynamic screening results showed that with CO and H_2, the exothermic reduction reaction can provide the necessary heat for the decomposition of $MgSO_3$ when operating below 700°C for CO and below 500°C for H_2. Therefore, if favorable kinetics exist at those temperatures, the fuel required to produce the reducing gas would be the only energy required by the calcination step.

More detailed heat balances were made for the calcination step for four reductant cases, as shown in Table 2-3. It is seen that H_2S may be eliminated as it must be heated to 1325°C and the overall reaction is decidedly endothermic. The high temperature non-catalytic option also requires an input temperature higher than the output, in the kinetically viable range of greater than 900°C.

The catalytic process is attractive for a variety of reasons. First, there is no external heat requirement for the catalytic process option. As shown in Table 2-4, CO and H_2 require temperatures in excess of 900°C to reduce SO_2 to sulfur. Methane will not reduce SO_2 to sulfur for $T < 1200°C$ except in the presence of a catalyst. With these high temperatures in the calciner, there is the potential for "dead burning" of the MgO. The "dead-burned" form of MgO, called periclase, is unreactive. Another problem associated with the high temperatures necessary for a non-catalytic process would be the need to use exotic materials of construction. Above 600°C, special materials of construction would probably be necessary.

A catalytic SO_2 reduction process can operate at temperatures in the 400-450°C range. This eliminates many of the problems related to high temperature operation. However, with a catalytic process, there will probably be a reactor effluent solid/solid separation problem. Several mechanical options are available which are probably capable of solving this problem. Some of these options are discussed briefly in Section 2.4.

TABLE 2-3

PROCESS OPTION TEMPERATURES, STAGE 2 OF FLUIDIZED BED

Reductant	Gas Effluent Temperature (°C)	Gas Feed to Stage 2 (°C)
Air-Blown Gasifier:		
Catalytic	550	450
Noncatalytic	900	1130
Oxygen-Blown Gasifier:		
Catalytic	900	1050
Noncatalytic	800	780
H_2S Gasifier:		
Catalytic	550	1325

TABLE 2-4

SUMMARY OF MINIMUM TEMPERATURES FOR REACTION

Reaction	Non-Catalytic Temperature (°C)	Catalytic Temperature (°C)	Catalyst*
$MgSO_3$ Decomposition	550	450-500	Iron Bauxite Iron and Chromium Oxides
CH_4 Reduction	1200	800	Bauxite Reduced Alunite
CO Reduction	Over 950	400	Bauxite Activated Alumina Metal/Alumina
H_2 Reduction	Over 900	300-400	Bauxite Alunite
CO-H_2 Reduction	No Information	400	Bauxite Al_2O_3

---

* These are some of the catalysts for which a significant sulfur yield was reported. This list is not complete.

A noncatalytic process is attractive in its simplicity. There are no gas phase catalyst and attendant solid/solid separations problems. There is insufficient information available at this time to choose between a catalytic and a noncatalytic process, therefore, a process design was made for both.

For purposes of performing detailed process calculations, it was decided that a single catalytic reaction vessel would be employed in Radian's conceptual sulfur-from $MgSO_3$ process. The single vessel design was chosen so that the heat required for $MgSO_3$ decomposition reaction would be provided by the exothermic SO_2 reduction reaction. The noncatalytic decomposition of $MgSO_3$ was also carried out in a single vessel.

A brief investigation was made of the possibility of using an initiator to start the homogeneous SO_2 reduction at lower temperatures. For example, hydrogen peroxide could provide OH radicals.

$$H_2O_2 + M = 2OH + M$$

The known rapid reaction with H_2 would provide H atoms.

$$OH + H_2 = H_2O + H$$

However, a consideration of the possible intermediate steps indicates that there is not a low activation energy pathway for overall reaction of SO_2 reduction to elemental sulfur. The reaction

$$SO_2 + H = SO + OH$$

is central to such a scheme, but it is endothermic by 31 kcal. An activation energy of 36 kcal is thus indicated, so that the homogeneous reaction could not occur in the lower temperature range even if initiated by an external radical source. Rather, a temperature of the order of 900°C would be required, just as with initiation by strictly thermal radicals.

2.4 Equipment Considerations

In this section pertinent operating characteristics of several different types of gas/solid contacting devices are examined. This analysis emphasizes those features of each device which relates to its suitability for use as a $MgSO_3$ regeneration reactor. Key considerations in this analysis are the ability of the contactor to promote efficient contact between $MgSO_3$ solids and the reducing gas, heat transfer characteristics, operability, and safety. The reactor types which were considered include rotary kilns, multiple hearth furnaces, rotary grate and flash roasters, and fluidized beds. These reactor types were screened to determine which configuration was most suitable from the point of view of accomplishing the calcination and reduction steps in a single reaction vessel. The key features of each reactor type are summarized below.

A rotary kiln is an insulated metal cylinder that rotates upon suitable bearings and is slightly inclined to the horizontal. Hot gases are used to heat the solid materials and to carry away product gases from the decomposed solid. In rotary kilns there is much less gas-solid contacting than in fluidized units. In normal operation the kiln seals allow some leakage of air, thus preventing operation under pressure or vacuum. Special seals are required in processes which must avoid problems associated with the entrance of outside air.

Multiple hearth furnaces consist of a number of annular sloped beds mounted one above the other. Feed material entering the top of the furnace falls from hearth to hearth as a result of the movement of rabble arms. Hot gas flows countercurrently upward through the hearths. Because of the poor gas-solid mixing characteristics of this type of furnace, a high consumption of fuel and a low concentration of SO_2 in the product gas is generally obtained when this type of contactor is employed in the smelting industry.

Flash roasters are generally used when the gas/solid reaction of interest is controlled by surface phenomenon or when the solid particles are very small so that heat and mass transfer from the interiors are very rapid. This type of furnace usually consists of a brick lined cylindrical shell, which encloses a relatively large combustion chamber, having one or two collecting and desulfating hearths at the base of the chamber and one or two drying hearths under these calcining hearths. The operation of the flash roaster resembles the burning of powdered coal in a furnace in that the solid concentrate is normally injected into the combustion chamber through entrainment in a stream of air.

Fluid bed reactors are often employed when using reasonably small granular or powdery feed materials. However, fluidizing $MgSO_3$ crystals may be a problem because of the extremely small particle size involved - on the order of 10 micrometers. Fluid bed operation generally results in the attrition of particles and high entrainment losses, in which case recovery equipment such as cyclones would be needed. The extremely small particle size of the $MgSO_3$ would probably lead to severe entrainment problems. It is generally concluded that particles distributed in size between 30-225 micrometers are the best for smooth fluidization. Small particles (less than 10 micrometers) frequently agglomerate. This can result in the formation of large lumps in the bed. $MgSO_3$ particles approach the lower limit for use in a fluid bed reactor.

A newly developed circular grate pelletizer/roaster which might avoid some of the problems associated with fluid bed operation has been developed by McKee (IA-003). This circular grate apparatus features a horizontal, washer shaped hearth which consists of a large number of metallic grate elements. The entire structure, which is mounted on a single center-support bearing assembly, slowly rotates through four operating zones. Presently, as it is used in an iron-ore pelletizing process, the four operating zones are feed/unloading, drying, induration, and cooling. These operating zones could probably be changed to accommodate a different type of operation. In its existing application, a single air stream flows successively through the four operating zones. This promotes efficient heat utilization. The favorable characteristic of this unit is its potential ability to pelletize the $MgSO_3$ crystals before calcination. This may be a method of avoiding the problems which would be associated with a fluid bed reactor. Also the grate could carry a layer of fixed bed, gas phase catalyst thus avoiding the solid/solid separation problem.

In spite of these potentially severe particle carryover problems, the superior heat and mass transfer characteristics of fluidized beds are significant factors which make this contactor type attractive for this application. In addition, a fluidized bed is one of the simplest models for making process calculations. For this reason a fluidized bed was the reactor type which was assumed to be employed in the calcination/reduction section of Radian's conceptual sulfur from $MgSO_3$ process which is described in Section 3.0. Even through the use of this type of contactor is assumed here, it must be recognized that potential solids carryover problems do exist with this approach.

The backmix characteristics of a fluid bed reactor (relative to the solid phase) lead to non-uniform residence times of solids in the reactor. For this reason, staging is probably desirable from the point of view of achieving high, uniform conversion levels. In the process design portion of this study, the use of a two-stage fluidized bed reactor was assumed.

As discussed in the previous section, the use of a catalytic process for the combined calcination/reduction step is desirable because of the high temperatures which would be associated with the non-catalytic process option. This leads to potential MgO/catalyst separation problems, however.

The conclusions which were reached as a result of this analysis can be summarized as follows. Conceptually, it is desirable to accomplish the calcination and reduction steps which must occur on the "front end" of this process in a single catalytic reaction vessel. This approach appears to be feasible, however, two potentially significant problem areas are apparent. The extremely small sizes of the $MgSO_3$ feed particles involved will probably lead to severe dusting problems. Also, if the catalytic process is used, a catalyst/MgO solid/solid separation step will probably be required. Although neither of these problems appears to be insurmountable, they will have to be dealt with if further development of this process is attempted.

Noncatalytic options have also been process engineered because it is felt that it is too early to make a confident decision as to the best course of action.

3.0 PROCESS DESCRIPTIONS

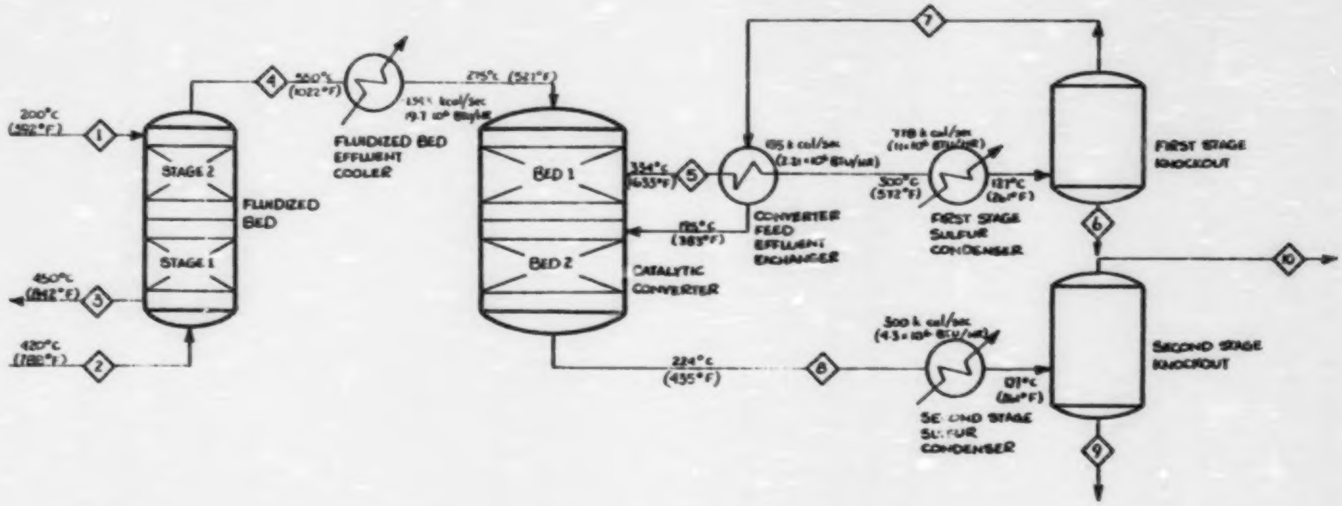
Two processes were investigated, i.e., catalytic and noncatalytic. For the catalytic process the reducing gas was produced in an air blown gasifier. Two cases were considered for the noncatalytic process. They were reducing gases from an oxygen blown gasifier and from an air blown gasifier.

Hydrogen sulfide was not considered in this step because the heat requirement was judged to be too high. A 1000 Mw power plant burning 2.3% sulfur coal was used as the basis for the design calculations. A flue gas sulfur removal efficiency of 90% was assumed. Given these assumptions, a $MgSO_3/MgSO_4$ feed rate of 75.85 g-moles/sec (760 tons/day) was determined.

The inlet $MgSO_3/MgSO_4$ feed rate was derived from the design of an SO_2 removal system for Philadelphia Electric's coal-fired Eddystone Station (120 Mw) burning 2.3% sulfur coal (average) with a sulfur removal of 90% (EN-125). The flow rate was linearly scaled to calculate $MgSO_3/MgSO_4$ production rates for a 1000 Mw plant. The percent of $MgSO_4$ in the feed was increased from 3.6% to 5.0%. The inlet $MgSO_3/MgSO_4$ (and the outlet MgO) flow rate was calculated to be 75.85 g-moles/sec. This yields 264,211 kg/day of MgO.

3.1 Catalytic Process Description

Based upon the results of the literature survey and thermodynamic screening subtasks, a process arrangement was developed which appears to be a technically feasible method of producing sulfur from magnesium sulfite. This process arrangement, which incorporates the desirable features discussed in previous sections, is shown in Figure 3-1. A low Btu syngas is used as the reducing agent.


200°C
(392°F)
1
STAGE 2
STAGE 1
FLUIDIZED
BED
450°C
(842°F)
3
420°C
(788°F)
2
4
550°C
(1022°F)
1337 kcal/sec
19.1 10⁶ Btu/hr
FLUIDIZED BED
EFFLUENT
COOLER
275°C (527°F)
BED 1
BED 2
CATALYTIC
CONVERTER
334°C
(633°F)
5
155 k cal/sec
(2.21×10⁶ Btu/hr)
CONVERTER
FEED
EFFLUENT
EXCHANGER
195°C
(383°F)
300°C
(572°F)
778 k cal/sec
(11×10⁶ BTU/HR)
127°C
(261°F)
FIRST STAGE
SULFUR
CONDENSER
7
FIRST STAGE
KNOCKOUT
6
10
224°C
(435°F)
8
300 k cal/sec
(4.3×10⁶ BTU/HR)
127°C
(261°F)
SECOND STAGE
SULFUR
CONDENSER
SECOND STAGE
KNOCKOUT
9

COMPONENT (g-moles/sec)	MW	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩
N_2	28.02		155.33		155.99	155.99		155.99	155.99		155.99
CO	28.01		75.21		0.04						
CO_2	44.01		16.42		96.77	99.16		99.16	99.18		99.18
H_2	2.016		45.32		0.08						
H_2O	18.016		24.96		63.85	81.00		81.00	88.01		88.01
CH_4	16.04		7.55								
NH_3	17.03		1.31								
H_2S	34.08		2.30		25.74	8.64		8.64	1.63		1.63
SO_2	64.06				13.12	4.34		4.34	.82		.82
COS	60.07				0.37	0.02		0.02			
* Elem S	32.06				38.92	66.16	65.00	.16	10.69	10.53	.16
$MgSO_3$	104.38	72.54									
$MgSO_4$	120.38	3.31									
MgO	40.312			75.85							
TOTAL		75.85	328.40	75.85	396.06	414.31	65.00	349.31	356.32	10.53	345.79
MOL WT		105.08	24.19	40.312	32.40	31.04	32.06	30.48	29.87	32.06	29.81
kg/sec		7.910	7.944	3.058	12.856	12.856	2.08	10.646	10.646	.338	10.308
Million lb/day		1.520	1.513	0.5824	2.450	2.450	.397	2.45	2.45	.0644	2.39
* S g-atoms/molecule					2.278	6.927	1.000	7.68	6.83	1.00	7.68

DRAWING NOTES:

1. STREAM COMPOSITIONS COMPUTED FROM EQUILIBRIUM CALCULATIONS AT 1.0 atm
2. BASIS FOR $MgSO_3$ FEED RATE:
   - 1000 MW POWER PLANT BURNING 2.5% SULFUR COAL
   - MAGOX SCRUBBING SYSTEM SULFUR REMOVAL EFFICIENCY: 90%
3. REDUCING GAS STOICHIOMETRY: 1.0
4. COMPLETE CONVERSION OF INLET $MgSO_3/MgSO_4$ TO MgO ASSUMED

FIGURE 3-1. CONCEPTUAL PROCESS FLOW DIAGRAM FOR PRODUCING ELEMENTAL SULFUR FROM $MgSO_3$ IN A CATALYTIC DECOMPOSER

The regeneration scheme which is proposed here includes a two-stage fluid bed reactor followed by a two-bed Claus reaction unit. A Claus unit is included in this design since the conversion of SO_2 to elemental sulfur that occurs in the fluid bed calcination reactor is only on the order of 50%. With the additional conversion, which is theoretically obtainable through the use of a two-stage Claus unit, a 97% overall conversion efficiency of SO_2 to S is theoretically possible.

A sulfur recovery rate of 2.43 kg/sec (231 tons/day) was calculated for the process scheme shown in Figure 3-1. If the effluent gas stream from the process were to be recombined with the power plant stack gas upstream of the scrubber, a slight additional improvement in the overall sulfur recovery efficiency of the overall sorption process would probably be realized. In a typical 1000 Mw power plant, this gas stream would increase the sulfur concentration in the stack gas by about 40 ppm.

The process arrangement calculations discussed in this section demonstrate that the calcination/reduction step can be performed without the addition of heat from an external source. The entire process is a net heat producer due to the exothermic reactions in the Claus reactor beds.

3.1.1 Catalytic Flow Sheet

The process flow sheet is shown in Figure 3-1. The solids enter the top of a two-stage fluidized bed. In the upper stage the majority of the calcination/reduction reactions take place. The lower stage serves to complete the solids reaction and to heat exchange the solids with the incoming reducing gases.

The gases laden with sulfur species are then cooled and passed through a catalyst bed. The exothermic reaction produces more elemental sulfur. Next, elemental sulfur is condensed and removed. The gases are reheated for additional catalytic sulfur conversion. The sulfur is again condensed.

3.1.2 Process Engineering Calculations

This section discusses the assumptions made and procedures used in developing the material and energy balance for the process arrangement shown in Figure 3-1.

The reducing gas used in the process was a typical air blown coal gasifier product gas (WA-199). The gas composition is shown in Table 3-1. This gas was chosen because (1) it contained significant amounts of CO and H_2 and (2) it represented one of the more difficult cases for producing the necessary heat in the calciner since 47.3% of the gas is nitrogen.

Other reducing gas sources could also be used. A typical composition for partial oxidation of Bunker C fuel oil (3.5 wt % S) using the Shell process (SH-200) is also listed in Table 3-1 for comparison. The two gases are similar enough so that no significant difference would be expected. One significant aspect is that the sulfur need not be removed from the reducing gas. Any high sulfur fuel may be used.

The first stage of the fluidized bed was assumed to act primarily as a heat exchanger with no chemical reaction between the species. The decomposition and reduction reactions were assumed to take place in the second stage of the fluidized bed. A temperature of 550°C was chosen for the second stage of the reactor. At this temperature all of the $MgSO_3/MgSO_4$ will decompose to MgO at equilibrium. The elemental sulfur yield in

TABLE 3-1

TYPICAL AIR BLOWN REDUCING GAS COMPOSITIONS

Component	Mole Percent	
	Coal	Bunker C
N_2	47.3	56.4
CO	22.9	21.6
CO_2	5.0	2.3
H_2	13.8	16.1
H_2O	7.6	3.2
CH_4	2.3	0.
NH_3	0.4	0.
H_2S	0.7	0.4

Sources: Coal: (WA-199)
Bunker C: (SH-200)

the reactor increases with decreasing temperature so that the lowest possible temperature within operating constraints was needed. Also, lower temperatures minimize material problems and energy requirements for the reactor. Higher temperatures, especially over 600°C, require the use of more expensive materials of construction and increase the amount of heat that must be supplied to the process by the reducing gas.

The temperature of the outlet MgO solids was calculated to be 450°C. Inlet $MgSO_3/MgSO_4$ from a drier would be at 200°C. A heat balance gave the inlet reducing gas temperature at 420°C. The exit solids must be further cooled for ease of handling. Should drying and dehydration be done off site, the feed temperature would be lower. A solids feed/effluent heat exchange loop could solve both feed heating and product cooling problems.

In calculating the amount of reducing gas needed at a stoichiometry of 1.0, it was assumed that H_2S, NH_3, and CH_4 would act as reducing agents even though it was noted in the literature survey that CH_4 would not react with SO_2 to any significant extent in a catalytic process operating below 800°C. Since the CH_4 content of the gas was low it does not have any appreciable influence one way or another. Methane was included as a reactant for computational ease.

Another potential problem with this process which is not indicated by the equilibrium calculations shown in Figure 3-1 is the formation of COS. At a 1.0 stoichiometry, equilibrium calculations imply that the formation of COS is not a problem. The kinetics of COS formation need to be investigated, however, before it can be stated with certainty that COS is not a problem. The literature survey reported that COS could be formed in large or small amounts when SO_2 and CO are reacted depending on the operating conditions of the reactor.

Of the total sulfur in the gases leaving the reducing calciner only about 50% is in the form of elemental sulfur. A lower temperature is required for further conversion. The gases are therefore cooled and sent to a catalytic converter.

The catalytic converter beds were designed to operate 25°C above the dewpoint of sulfur since liquid sulfur condensate will poison the converter catalyst (GA-155). In each case, the converter inlet temperature was chosen such that the exothermic heat of reaction in the converter beds was sufficient to keep the gas temperature above the sulfur dewpoint.

The system pressure was assumed to be 1.0 atm for all of the equilibrium calculations. In actual fact, the pressures throughout the system would probably vary from 1-2 atmospheres. The results of the equilibrium calculations would probably not be significantly changed by pressure differences of this magnitude.

The gas phase elemental sulfur must be removed to shift the reaction equilibrium in favor of further formation of elemental sulfur. This is accomplished by condensing molten sulfur.

Sulfur condensation calculations were made by assuming that, except for the elemental sulfur species (S_2, S_3, $\cdots S_8$), the gas phase composition remained fixed. A sulfur condenser temperature of 127°C (261°F) was chosen so as to be 7°C above the freezing point. Additional elemental sulfur production by the Claus reaction is favored thermodynamically at 127°C; however, this will not happen because of the poor noncatalyst kinetics at this low temperature. While the 7°C approach in the sulfur condenser may have to be raised to avoid freezing problems, the overall sulfur recovery will not be significantly affected.

After the first stage of sulfur condensation the gases are heated so that the second catalytic bed exit temperature will be 224°C. This exit temperature was again selected so as to be slightly above the elemental sulfur dewpoint.

The sulfur is again condensed at 127°C. Elemental sulfur recovery is 97% of the sulfur entering the process. The off gases contain minor amounts of SO_2, H_2S, and S_x. These off gases may contain too many noxious components to discharge directly to the atmosphere. Incineration, additional catalytic conversion, recycle, etc., are options to be investigated.

3.1.3 Catalytic Fuel Requirements

The heat requirement for the process is calculated in two ways. The first way is intended to give an estimate of the efficiency of the reducing calcining process. The calculation is carried out in the following manner. An "equivalent" heat of combustion of the reducing gas is calculated for the reducing gas at the fluidized bed inlet temperature (420°C) going to combustion products of CO_2, $H_2O(v)$, $S(\ell)$, and N_2 at the temperature of the second stage sulfur condenser (127°C). Since the oxygen source is the $MgSO_3$, the oxygen for combustion is calculated at 200°C, the $MgSO_3$ inlet temperature.

The equivalent heat of combustion calculated in the above manner is distributed between the heat of calcination of $MgSO_3$, the heat of the gas phase reactions, and process heat rejection. The first two items are required and therefore define the efficiency of the process. Table 3-2 summarizes the process heat rejection loads. The reduction process thermal efficiency is 77%.

TABLE 3-2

ENTHALPY CONSIDERATIONS FOR THE PRODUCTION OF ELEMENTAL SULFUR FROM MAGNESIUM SULFITE

Equipment	Process Temperature (°C) Inlet	Process Temperature (°C) Outlet	Heat Rate (kcal/sec)
Fluidized Bed Effluent Cooler	550	275	-1343
First Sulfur Condenser	300	127	-778
Second Sulfur Condenser	224	127	-300
TOTAL			-2421
Equivalent Heat of Combustion of Reducing Gas			-10392

Process Thermal Efficiency $\frac{-10392 + 2421}{-10392} = 0.767$

The second way of looking at the heat requirement is by comparing the SO_2 control process fuel requirement with the power plant fuel requirement. Assuming a gasifier efficiency of 75% the heat rate to the gasifier is 13,900 kcal/sec. This is 2.0 percent of the power plant heat rate of 700,000 kcal/sec (based on 10,000 Btu/kwh). If the calcination and reduction steps were to be carried out separately, the fuel requirement for calcination would be added to the present reduction requirement. This additional heat would have to be rejected or used in some manner. Compared to separate calcination and reduction facilities, the use of simultaneous solids decomposition/SO_2 reduction will not only require less fuel but also a potentially lower capital investment because of less heat transfer surfaces.

The heat load for drying and dehydration will add one percent or so to either one or two step processes. The temperature level of the drying step is low (∿200°C) so that low level heat sources should be sought.

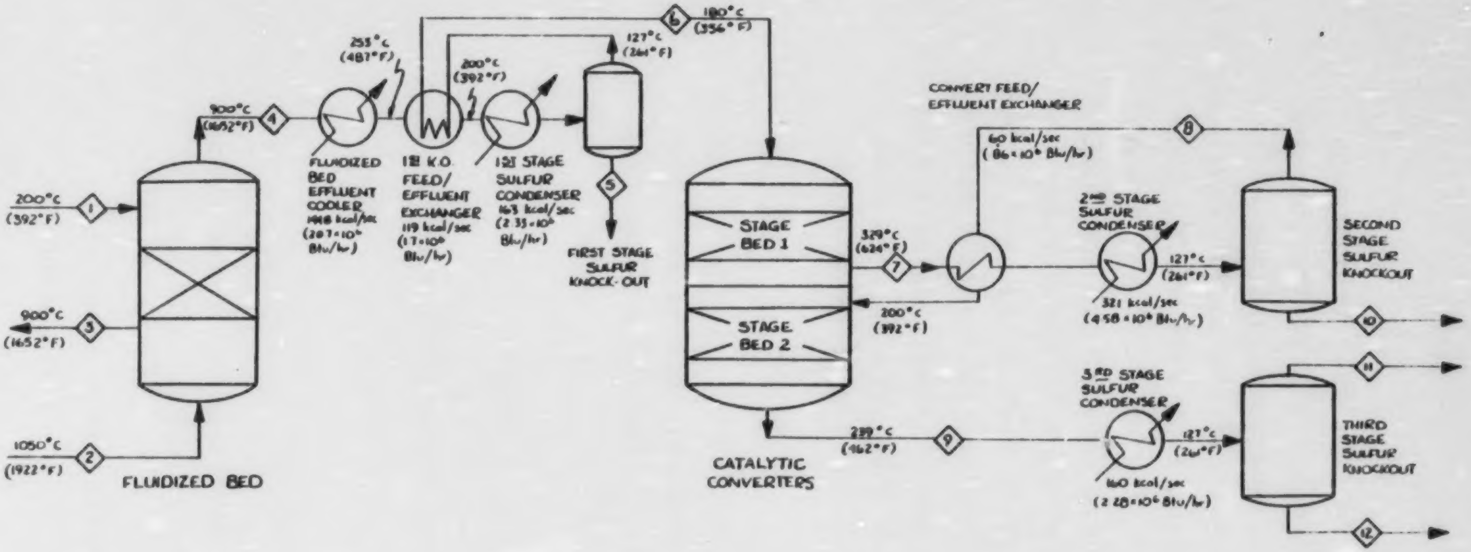
3.2 Noncatalytic Process

Two cases were investigated for noncatalytic processes.

3.2.1 Noncatalytic Flow Sheets

The first case was based upon a reducing gas from an oxygen blown gasifier. This case is shown in Figure 3-2.

Because the gas phase reaction is noncatalytic, the fluidized bed exit temperature is 900°C. As discussed in Section 2, the formation of S_2 in the gas phase reduces the heat available for calcination of $MgSO_3$. The result is that


200°C
(392°F)
1
900°C
(1652°F)
3
1050°C
(1922°F)
2
FLUIDIZED BED
900°C
(1652°F)
4
FLUIDIZED BED EFFLUENT COOLER 1418 kcal/sec (20.7×10⁶ Btu/hr)
253°C
(487°F)
1st K.O. FEED/ EFFLUENT EXCHANGER 119 kcal/sec (1.7×10⁶ Btu/hr)
200°C
(392°F)
1st STAGE SULFUR CONDENSER 163 kcal/sec (2.35×10⁶ Btu/hr)
127°C
(261°F)
5
FIRST STAGE SULFUR KNOCK-OUT
6
180°C
(356°F)
STAGE BED 1
STAGE BED 2
CATALYTIC CONVERTERS
329°C
(624°F)
7
200°C
(392°F)
239°C
(462°F)
9
CONVERT FEED/ EFFLUENT EXCHANGER
60 kcal/sec
(.86×10⁶ Btu/hr)
8
2nd STAGE SULFUR CONDENSER
321 kcal/sec
(4.58×10⁶ Btu/hr)
127°C
(261°F)
SECOND STAGE SULFUR KNOCKOUT
10
3rd STAGE SULFUR CONDENSER
160 kcal/sec
(2.28×10⁶ Btu/hr)
127°C
(261°F)
THIRD STAGE SULFUR KNOCKOUT
11
12

COMPONENT g/moles/sec	MW	1	2	3	4	5	6	7	8	9	10	11	12
N_2	28.02		2.40		2.40		2.40	2.40	2.40	2.40		2.40	
CO	28.01		76.20		2.63		2.63	-	-	-		-	
CO_2	44.01		6.70		80.36		80.36	83.79	83.79	83.80		83.80	
H_2	2.016		74.00		1.86		1.86	.002	.002	-		-	
H_2O	18.016		20.70		77.47		77.47	91.01	91.01	95.83		95.83	
CH_4	16.04		0.91		-		-	-	-	-		-	
NH_3	17.03		-		-		-	-	-	-		-	
H_2S	34.08		1.20		18.39		18.39	6.70	6.70	1.89		1.89	
SO_2	64.06		-		11.83		11.83	3.34	3.34	0.93		0.93	
COS	60.07		-		0.82		0.82	0.01	0.01	-		-	
* ELEM S	32.06		-		46.01	45.92	0.091	21.08	0.089	8.14	21.811	0.087	8.053
$MgSO_3$	104.38	72.54	-		-	-	-	-	-	-	-	-	-
$MgSO_4$	120.38	3.31	-		-	-	-	-	-	-	-	-	-
MgO	40.312	-	-	75.85	-	-	-	-	-	-	-	-	-
TOTAL		75.85	181.11	75.85	241.77	45.92	195.85	208.33	187.34	192.99	21.811	184.94	8.053
MOL WT		105.08	16.88	40.312	33.03	32.06	33.26	31.27	31.17	30.40	32.06	30.33	32.06
Kg/sec		7.910	3.074	3.058	7.986	1.472	6.514	6.514	5.840	5.840	0.699	5.608	0.258
Mill lbs/day		1.518	.5855	0.5824	1.521	0.280	1.241	1.245	1.112		0.133	1.068	0.049
*S g-atoms/molecule		-	-		2.01	-	7.60	6.88	7.60	7.34	-	7.60	-

DRAWING NOTES:

1. STREAM COMPOSITIONS COMPUTED FROM EQUILIBRIUM CALCULATIONS AT 1.0 atm
2. BASIS FOR $MgSO_3$ FEED RATE:
   - 1000 MW POWER PLANT BURNING 2.5% SULFUR COAL
   - MagOx SCRUBBING SYSTEM SULFUR REMOVAL EFFICIENCY: 90%
3. REDUCING GAS STOICHIOMETRY: 1.0
4. COMPLETE CONVERSION OF INLET $MgSO_3/MgSO_4$ TO MgO ASSUMED

FIGURE 3-2. NONCATALYTIC REDUCTION, OXYGEN-BLOWN GASIFIER

the inlet gas must be supplied at a higher temperature. A process alternate might be to supply extra reductant and air for combustion to supply the extra heat.

The higher exit temperature for the noncatalytic process has taken the process away from the minimum equilibrium sulfur formation range of 550-700°C. This results in the need for a sulfur condenser and knockout ahead of the first stage catalytic converter. The noncatalytic reaction temperature was selected based on limited laboratory data. Further bench scale studies should address this point. Reaction initiation will be aided by the reducing gas feed to the calcining bed being 150°C higher than the final bed temperature.

After the elemental sulfur has been condensed and removed, the gas is reheated and sent to the first stage catalytic converter. Equilibrium limits the conversion. Therefore, elemental sulfur is again condensed and the gases returned to a catalytic converter. The elemental sulfur formed is again condensed. The waste gases are sent to final disposal.

3.2.2 Noncatalytic Process Design

All calculations were carried out at one atmosphere pressure absolute. Overall removal of elemental sulfur is about 96%. Design considerations of the catalytic recovery units are similar to the catalytic fluidized bed system.

3.2.3 Noncatalytic Fuel Requirements

The heat requirements for the noncatalytic (fluidized bed) process were calculated in the same manner as for the catalytic process. The process heat rejection duties and equivalent heat of combustion are given in Table 3-3. The reduction process thermal efficiency is 80.3%.

TABLE 3-3

ENTHALPY CONSIDERATIONS FOR THE PRODUCTION OF ELEMENTAL SULFUR FROM MAGNESIUM SULFITE NONCATALYTIC PROCESS

Equipment	Process Temperature (°C) Inlet	Process Temperature (°C) Outlet	Heat Rate (kcal/sec)
First Fluidized Bed Effluent Cooler	900	253	-1448
Final Fluidized Bed Effluent Cooler	200	127	-163
Final First Bed Effluent Cooler	286	127	-321
Second Bed Effluent Cooler	239	127	-160
TOTAL			-2092

"Equivalent" Heating Value of Reducing Gas -10640

$$\text{Thermal Efficiency} = \frac{-10640 + 2092}{-10640} = 0.803$$

The fuel to the gasifier represents 2.0% of total power plant heat rate if the gasifier is again assumed to operate at 75% efficiency.

3.2.4 Noncatalytic-Air Blown Gasifier Case

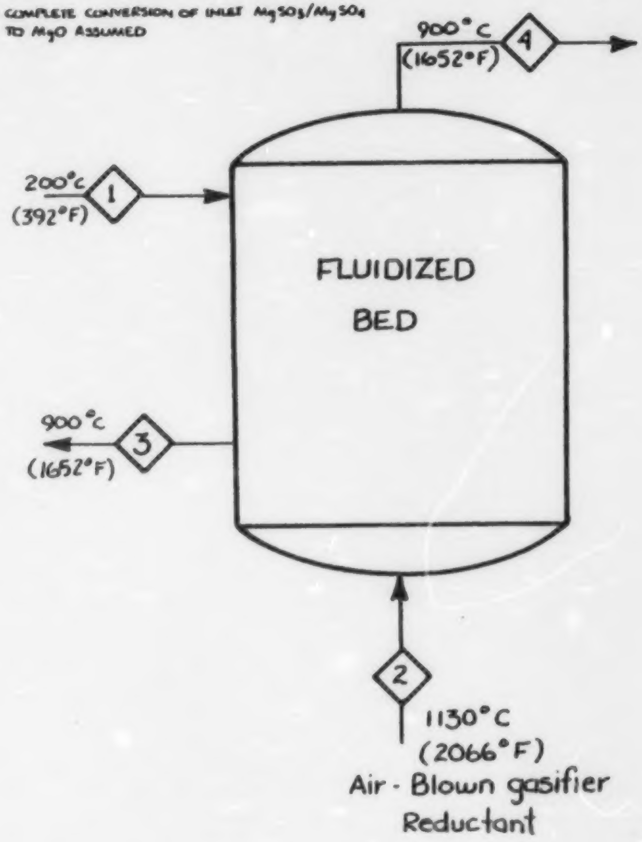
Reducing gases from an air blown gasifier were also considered. The process flow diagram for the reducing calciner is shown in Figure 3-3.

In order to maintain the outlet temperature at 900°C an inlet reducing gas temperature of 1130°C (2066°F) is required. This was considered to be unreasonably high so further calculations were not made in this feasibility study. If excess reducing gas and air were introduced to provide extra heat, a lower temperature could be used and the process might look attractive.

At any rate, the process arrangement would be similar to Figure 3-2 with compositions similar to those given in the flow diagram of Figure 3-1.

DRAWING NOTES:

1. STREAM COMPOSITIONS COMPUTED FROM EQUILIBRIUM CALCULATIONS AT 1.0 atm
2. BASIS FOR $MgSO_3$ FEED RATE:
   - 1000 MW POWER PLANT BURNING 2.3% SULFUR COAL
   - Magox SCRUBBING SYSTEM SULFUR REMOVAL EFFICIENCY: 90%
3. REDUCING GAS STOICHIOMETRY: 1.0
4. COMPLETE CONVERSION OF INLET $MgSO_3/MgSO_4$ TO MgO ASSUMED


900°C
(1652°F)
4
200°C
(392°F)
1
FLUIDIZED
BED
900°C
(1652°F)
3
2
1130°C
(2066°F)
Air - Blown gasifier
Reductant

COMPONENT g/moles/sec	MW	1	2	3	4
N_2	28.02		155.33		155.98
CO	28.01		75.21		3.71
CO_2	44.01		16.42		94.56
H_2	2.016		45.32		2.05
H_2O	18.016		24.96		71.54
CH_4	16.04		7.55		
NH_3	17.03		1.31		
H_2S	34.08		2.30		16.05
SO_2	64.06				11.37
COS	60.07				0.91
* ELEM S	32.06				49.82
$MgSO_3$	104.38	72.54			
$MgSO_4$	120.38	3.31			
MgO	40.312			75.85	
TOTAL		75.85		75.85	405.99
MOL. WT.		105.08		40.312	31.667
Kg/sec.		7.970		3.058	12.856
MILL. lbs/day				0.5824	2.449
*S $\frac{\text{g-atoms}}{\text{molecule}}$					2.009

FIGURE 3-3 NONCATALYTIC REDUCTION AIR-BLOWN GASIFIER

4.0 RESULTS AND CONCLUSIONS

In this section the significant results of this study are summarized. The conclusions generated as a result of this effort are also discussed.

4.1 Summary of Results

Subtask 1 - Literature Survey

From the literature survey it was concluded that probably the reaction mechanism for producing elemental sulfur from $MgSO_3$ involved two steps. The first step was decomposition of $MgSO_3$ to MgO and SO_2. The second step was reaction of SO_2 with an appropriate reducing gas. No evidence was found to support the existence of a direct gas-solid reaction for producing elemental sulfur from $MgSO_3$.

Descriptions of several commercial processes which yield elemental sulfur as a product of reducing gas reactions with SO_2 were found in the literature. CO, H_2, and methane are all being used in this application currently. Since the conditions for $MgSO_3$ calcination are approximately known, the use of this two-step approach to elemental sulfur production definitely appears to be technically feasible.

Subtask 2 - Thermodynamic Screening

In the thermo screening subtask, chemical reaction equilibrium and heat balance calculations were used to define the effects of temperature and reducing gas stoichiometry upon the equilibrium sulfur yield which would result from the reaction of $MgSO_3$ with four different reducing gases: H_2, CO, CH_4, and a H_2/CO mixture. The highest equilibrium sulfur yields were obtained in cases where CO was used as the reductant. Significant (> 50%) conversion of SO_2 to sulfur was obtained with all four gases under optimum conditions.

Among the significant conclusions which were reached as a result of this effort are the following.

(1) At high stoichiometries, the two reducing gases containing carbon (CH_4 and CO) showed large solid carbon formation tendencies. This indicates that coke formation at the point of reducing gas injection to the calcination reactor is a potential problem.

(2) At high stoichiometries, sulfur has a thermodynamic tendency to react with excess H_2 to form H_2S and excess CO to form COS. This indicates that, from an equilibrium point of view, no incentives exist for operating with a large excess of reducing gas. It should be noted that this conclusion does not take into account the kinetic factors that may be involved in these reaction systems.

(3) The enthalpy data which were generated along with these equilibrium results are also significant. Since the $MgSO_3$ decomposition reaction is endothermic and SO_2 reduction reactions are exothermic, heat transfer considerations make it desirable to accomplish both of these conversion steps in a single reaction vessel. The heat balance calculations which were performed as part of this

subtask indicate that the adiabatic operating temperature of the calcination reactor is in the 700-1000°C range when CO is used as the reductant and between 500 and 700°C for H_2. Each reaction system is exothermic (requires heat removal) at lower operating temperatures. The heat requirements for H_2-CO mixtures fell between those of the two pure component cases. The methane system was endothermic at all temperatures considered ($T \leq 1000°C$).

Based upon the findings of the literature survey and thermo screening subtasks, it was concluded that an attractive conceptual approach to the production of elemental sulfur from $MgSO_3$ appears to involve the use of CO or H_2 in a catalytic $MgSO_3$ decomposition process. This conclusion is based upon a variety of factors.

(1) Noncatalytic process options require high reaction temperatures and high feed temperatures for adiabatic operation. This presents materials of construction and external heat transfer problems.

(2) With methane, even when a catalyst is used, high reaction temperatures and an external source of heat would be required. This makes CO and H_2 more desirable as potential SO_2 reductants.

(3) Low calcination temperatures should maximize MgO product reactivity.

The problem of separating the gas phase SO_2 reduction catalyst from MgO product is an incentive for a noncatalytic gas phase SO_2 reduction reaction. One of the main objections, high inlet reducing gas temperatures, could be overcome by introducing excess reducing gas and air to obtain extra heat of combustion. There is not enough information presently available to make a choice between either catalytic or noncatalytic composition options.

The use of H_2S does not appear to be feasible since external heat transfer would be required. Burning excess H_2S to provide the extra heat is unattractive.

Subtask 3 - Specification of Process Arrangement

Based upon the results of the first two subtasks, process arrangements which appear to represent technically feasible approaches to the production of elemental sulfur from $MgSO_3$ were developed. A major portion of this effort was concerned with an evaluation of different types of solid-gas contactors to determine which reactor type would be most suitable for use as a calcination/reduction reactor.

It was concluded that the superior heat and mass transfer characteristics of fluidized beds make this contactor attractive for use in this application. For this reason, a fluidized bed was assumed to be used to accomplish the calcination step in the conceptual process arrangement which was developed in this subtask. Potential problem areas which were identified as being associated with this reactor design included: (1) MgO solids entrainment problems and (2) catalyst MgO solid separation problems.

Since the equilibrium sulfur yield in the calcination reactor outlet gas was only on the order of 50%, a two-stage catalyst reaction unit was also assumed to be used with this process in order to obtain additional sulfur recovery.

As a result of these considerations, the overall processing scheme which resulted from Radian's effort on this subtask consisted of the following general steps.

(1) Calcination/reduction of $MgSO_3$ to produce regenerated MgO solids and a product gas containing elemental sulfur, SO_2, H_2S, CO_2, and minor amounts of COS.

(2) Further conversion of residual H_2S and SO_2 to produce additional sulfur in a two-stage Claus reaction unit. Condensation was provided between the first and second stages of the Claus unit. Product sulfur was again condensed after the second stage.

Subtask 4 - Process Analysis

In this subtask, detailed engineering calculations were made to determine the equilibrium sulfur yield which was theoretically attainable using the process arrangements developed in the previous subtask. These calculations showed that a 96-97% overall recovery of elemental sulfur was possible.

Heat balance calculations indicated that the energy requirements of this regeneration process option represent about 2% of the total fuel energy supplied to the power station.

4.2 Conclusions

Based upon the results of the four program subtasks as summarized in the previous section, it was concluded that the production of elemental sulfur as a by-product of MgO regeneration appears to be technically feasible. Current literature indicates that a two-step mechanism involving $MgSO_3$ calcination followed by SO_2 reduction is possible. The most favorable approach to accomplishing this conversion appears to be one in which the initial calcination and reduction steps are allowed to take place in a single reaction vessel. This approach is desirable because it minimizes the external energy requirements of the process and eliminates heat transfer surfaces.

Two processes were investigated. The first process involving low temperature (550°C) calcining in the presence of a gas phase SO_2 reduction catalyst. The second process involved a higher temperature (900°C) calcining with no gas phase SO_2 reduction catalysts present. Both of these process options require further catalytic gas phase reactions to maximize elemental sulfur recovery.

It was concluded that if possible the SO_2 reduction step should be accomplished in the presence of a catalyst. This will make it possible to operate the regeneration reactor adiabatically and at a lower temperature than would be possible with a noncatalytic process. The major disadvantage of the catalytic process is the associated solid:solid separation problem.

Process engineering calculations indicate that high equilibrium sulfur yields are possible with reasonable fuel requirements. Although no reports of this approach to MgO regeneration were found in the literature, this approach appears to be technically feasible.

5.0 RECOMMENDATIONS

Further study of the feasibility of producing elemental sulfur from $MgSO_3$ should be directed mainly toward the potential problem areas which were identified as a result of this study. Basically, it appears that most of the problems associated with the conceptual process which is proposed here are concerned with the operation of the reducing calciner. The technology associated with the treatment of the calciner effluent gas is well understood since the requirements of that conversion step are similar to those which are currently being handled by existing Claus reaction units. Likewise, the production of a suitable reducing gas is not anticipated to be the source of significant problems since a wide variety of reducing gases are being produced on a commercial scale at present. In theory, the effluent gas from any partial oxidation process would be a suitable reducing gas for feed to the calcination reactor.

The next step should be that of generating data leading to the design and operation of a bench-scale reducing calciner. The four major problem areas associated with the design and operation of the calcination reactor which need to be studied further are summarized below:

- particle properties and size,
- solid decomposition reactions,

- kinetics of the reducing gas/SO_2 reactions with emphasis on heat transfer related problems,

- evaluation of available catalysts for attrition resistance and activity in the calcination environment.

These phenomena must be understood and quantified so that an engineering decision as to the type of reactor best suited to this application can be made. Major mechanical problems anticipated are:

- handling of very fine particles (1-10 microns),
- separation of MgO/catalyst mixtures.

After determining the reaction and heat transfer kinetics, a selection of reactor type can be made to best incorporate a solution to the above mechanical problems. This reactor should be tested if possible at a bench-scale using bottled reducing gases.

The above factors related to the noncatalytic process, e.g. solid $MgSO_3$ decomposition and gas phase kinetic, should be investigated in the temperature range of interest. There is some possibility that a decision could then be made as to whether a catalytic or a noncatalytic reducing calciner could be chosen.

Assuming the process still appears favorable, the next phase should involve some type of pilot plant. A 20,000 nm^3/hr (10,000 scfm) flue gas stream containing 2,000 ppm SO_2 could produce about one metric ton/day of elemental sulfur. It is essential that a $MgSO_3$ stream of this size be treated and elemental sulfur produced. It would be highly desirable to coordinate this pilot study with an existing scrubbing facility to include magnesium sulfite drying and MgO recycle. On-site production of reducing gas is probably not necessary and perhaps not even desirable.

The final step in this process development effort would, of course, be a prototype unit in which all system components would be tested in a closed loop operating mode.

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APPENDIX A

TECHNICAL NOTE 200-045-31-01a

"LITERATURE SURVEY ON THE RECOVERY OF ELEMENTAL SULFUR FROM MAGNESIUM SULFITE"

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LITERATURE SURVEY ON THE RECOVERY OF ELEMENTAL SULFUR FROM MAGNESIUM SULFITE

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Revised
2 December 1975

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1.0 INTRODUCTION

This technical note describes the results of a literature survey conducted to gather chemical and engineering data pertaining to processes for producing sulfur from magnesium sulfite. This information was needed to provide a basis for subsequent thermodynamic screening studies, selection of possible process arrangements, and calculation of process heat and material balances.

The first major section of this document discusses the chemistry of $MgSO_3$ decomposition and gas phase reactions involving sulfur products and reducing agents. Emphasis is on compilation and summary of the existing information rather than critical evaluation. Relatively few data were found concerning the direct reduction of $MgSO_3$. Considerable work has been done on the thermodynamics and kinetics of the gas phase reactions of interest.

The second major section of this document is concerned with existing commercial processes for production of sulfur from $MgSO_3$ or SO_2. Process schemes, equipment types and operating conditions are given. It should be noted that no existing process for direct conversion of $MgSO_3$ to sulfur was found. Once again, emphasis in this section is on description rather than critical evaluation.

2.0 CHEMISTRY OF ELEMENTAL SULFUR FORMATION FROM MAGNESIUM SULFITE

In the first stage of this program, the potential recovery of elemental sulfur from anhydrous magnesium sulfite was examined considering both one- and two-step approaches. A literature survey was conducted to identify the process chemistry options involved in each case. The decomposition and reduction of $MgSO_3$ will be important in either approach. Information found concerning thermodynamics, kinetics, and mechanisms of $MgSO_3$ reactions is presented in Section 2.1 of this technical note. The literature was surveyed using Chemical Abstracts from 1907 through June 1975.

It is likely that a two-stage mechanism will be most feasible. This will be based on reduction of sulfur dioxide resulting from $MgSO_3$ decomposition in the first step. Therefore, identification of available information concerning thermodynamics, kinetics, and mechanisms of SO_2 reduction chemistry was the second goal in the literature search. Since formation of hydrogen sulfide and other sulfur-containing gases may occur through side reactions, this aspect is also of concern. Because of the magnitude of information available in this broad area, the scope of the summary presented in Sections 2.2 through 2.4 is limited to key literature covered by Chemical Abstracts from 1967 to June 1975. Data contained in the abstracts were relied on in many instances.

2.1 Magnesium Sulfite Decomposition

Two hydrated forms of magnesium sulfite exist, the tri- and hexahydrates. Both can occur in MgO flue gas desulfurization systems.

Several experimental investigations of the heating behavior of the hexahydrate have been reported. In early work, Rammelsberg (2-1) reported a temperature of dehydration slightly above 200°C. At the same time he noticed an evolution of SO_2 due to the decomposition of the sulfite. This agrees with the observation of Foerster and Kubel (2-2) who found a loss of the water of hydration at 200°C with a simultaneous decomposition of the sulfite. These authors also reported a noticeable decomposition at 300°C without a complete loss of the water of hydration. Hagisawa (2-3) found a continuous transition from the trihydrate to the anhydrous salt.

Okabe and Hori (2-4) reinvestigated the decomposition behavior in 1959 using differential thermal analysis, X-ray diffractometry and infrared spectrometry. The DTA experiments were performed with 500 mg samples and heating rates of 3 and 5°C/min. The atmosphere was not clearly defined in the article. Evidently, the samples were heated in air. The X-ray and infrared experiments were performed after heating the samples under the same conditions as in the DTA experiments. Figures A2-1 through A2-3 show the results of this study. The first three molecules of water of hydration are lost in two steps at 60 and 100°C. The X-ray pattern of the compound heated to 100°C is remarkably different from the pattern at room temperature. At 200°C, the last three molecules of water of hydration are lost. The DTA plot shows a strong endotherm at this temperature. The

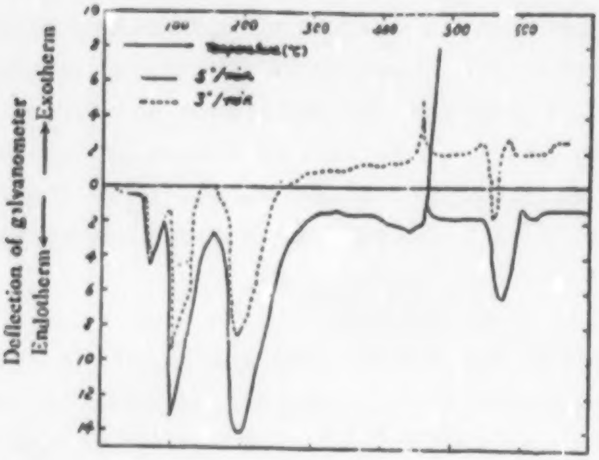


FIGURE A2-1. DIFFERENTIAL THERMAL ANALYSIS OF $MgSO_3 \cdot 6H_2O$ (2-4)

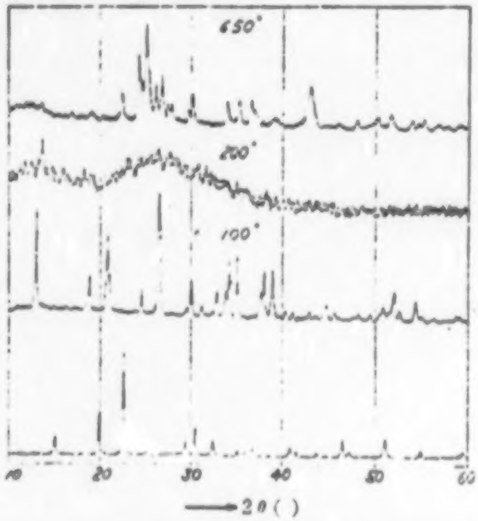


FIGURE A2-2. X-RAY DIFFRACTION PATTERN OF MAGNESIUM SULFITE AND ITS DECOMPOSITION PRODUCTS (2-4)

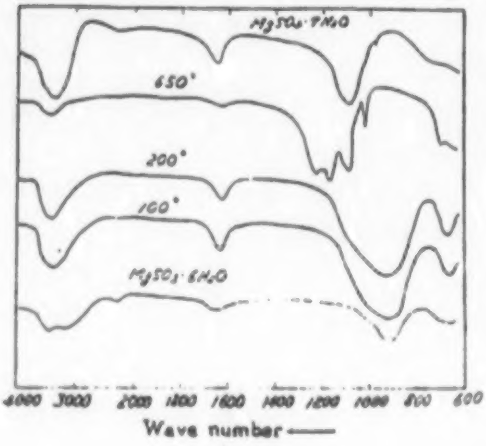


FIGURE A2-3. INFRARED ABSORPTION SPECTRA OF MAGNESIUM SULFITE AND ITS DECOMPOSITION PRODUCTS (2-4)

anhydrous phase is nearly amorphous as indicated by the X-ray diffraction pattern at 200°C. The exothermic peak in the DTA plot at about 480°C, as well as the endotherm at 560°C, are not clearly interpreted by Okabe and Hori. The authors mention in the article only that an oxidation and decomposition process must be involved. They base this statement on the fact that oxide and sulfate are the decomposition products. They consider the exotherm at 480°C as being the oxidation of magnesium sulfite, whereas the endothermic reaction at 560°C is the dissociation of the occluded sulfite. There are no reaction mechanisms proposed in the article.

Foerster and Kubel used quantitative analytical techniques to investigate the decomposition behavior of $MgSO_3 \cdot 6H_2O$ The hexahydrate was dehydrated in a stream of nitrogen at 250°C, and then heated to the desired reaction temperature. The gaseous and solid reaction products were analyzed for SO_2, free sulfur, sulfite, sulfate, and thiosulfate. The authors mention that no sulfide was found. The results are given in Table A2-1 and Figure A2-4. The following decomposition mechanism was proposed:

$$4MgSO_3 \rightarrow 2MgSO_4 + 2MgSO_2 \qquad (2\text{-}1)$$

$$\underline{2MgSO_2 \rightarrow MgS_2O_3 + MgO} \qquad (2\text{-}2)$$

$$4MgSO_3 \rightarrow 2MgSO_4 + MgS_2O_3 + MgO \qquad (2\text{-}3)$$

Parallel to these reactions, they assumed a decomposition of the sulfite,

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (2\text{-}4)$$

and a decomposition of the thiosulfate,

$$MgS_2O_3 \rightarrow MgSO_3 + S \qquad (2\text{-}5)$$

TABLE A2-1

DECOMPOSITION OF $MgSO_3$ AS FUNCTION OF TEMPERATURE

Heating Time One Hour (2-2)

Temp., °C	% S in Undecomposed Sulfite	% S in Sulfate	% S in Thiosulfate	% Total Sulfur in the Residue	% Elemental Sulfur in the Solid Residue	% S as SO_2 in the Effluent Gas	% Elemental Sulfur in the Effluent Gas	% Total Elemental Sulfur
300	84.7	7.3	2.5	98.0	3.5	2.9	-0.9	3.5
350	75.1	13.7	5.2	95.9	1.9	3.7	0.4	2.3
400	69.5	17.0	6.7	95.5	2.3	5.0	-0.5	2.3
450	67.5	17.0	6.7	93.2	2.1	6.4	0.4	2.5
500	52.5	23.3	5.7	80.7	0.8	12.9	6.4	7.2
550	3.6	27.9	--	31.4	-0.1	54.7	13.9	13.9

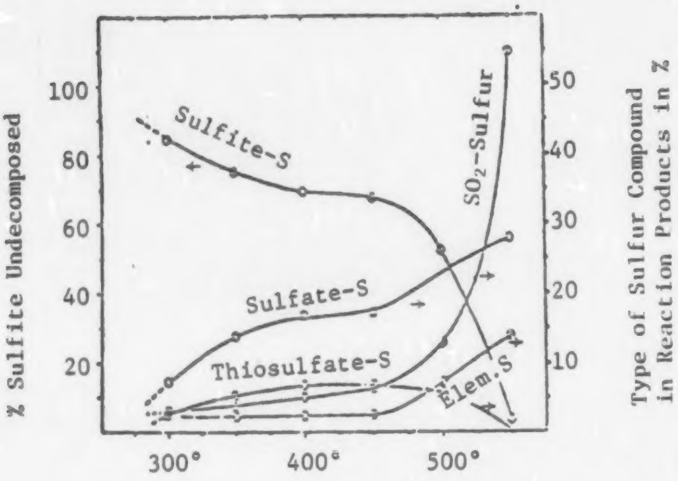


FIGURE A2-4
GRAPHIC PRESENTATION OF THE RESULTS SHOWN IN TABLE 2-1 (2-4)

Similar techniques were used by Ketov and Pechkovskii (2-5) to investigate the decomposition of $MgSO_3$. The magnesium sulfite was placed in a porcelain boat and ignited in a tube furnace in a stream of N_2 gas. The results are given in Table A2-2 and Figure A2-5.

TABLE A2-2
EFFECT OF TEMPERATURE ON THE DEGREE OF THERMAL DECOMPOSITION OF MAGNESIUM SULFITE IN A STREAM OF NITROGEN (2-5)

Temp., °C	% Conversion of S of $MgSO_3$				
	SO_2	MgS_2O_3	S_2	$MgSO_4$	TOTAL
300	0.7	2.1	2.0	5.7	10.5
350	2.1	3.6	2.6	8.8	17.1
400	5.7	4.8	3.1	10.8	24.4
450	16.3	5.3	3.8	12.9	38.3
500	36.8	4.5	5.2	14.9	61.4
550	68.5	0.0	8.4	17.5	94.4
600	88.2	0.0	3.9	7.8	99.9

Gas Flow Rate: 3.0 ℓ/hr

Test Time: 15 minutes

Sample Size: 0.5g

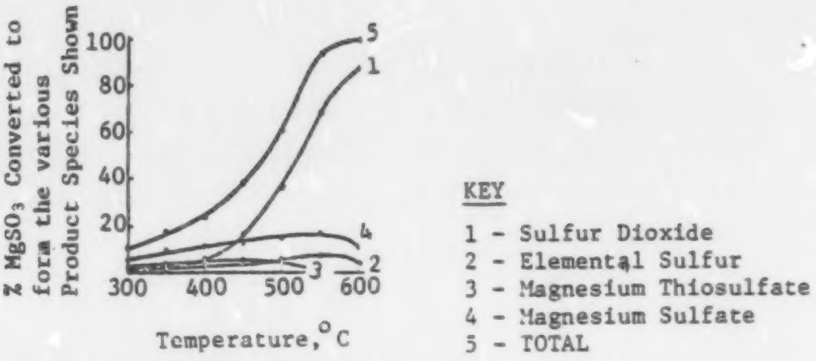


FIGURE A2-5
DEPENDENCE OF THE DEGREE OF DECOMPOSITION OF MAGNESIUM SULFITE ON TEMPERATURE IN A STREAM OF NITROGEN (2-5)

Ketov and Pechkovskii found the same decomposition products as Foerster and Kubel. They proposed, however, a different reaction mechanism. The sulfur dioxide is, according to Pechkovskii and Ketov, formed by the dissociation of magnesium sulfite according to the reaction:

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (2\text{-}4)$$

The presence of magnesium sulfate and sulfur in the solid products is explained by an oxidation of magnesium sulfite by sulfur dioxide under the conditions of the experiment according to the equation

$$2MgSO_3 + SO_2 = 2MgSO_4 + \tfrac{1}{2}S_2 \qquad (2\text{-}6)$$

To prove this, magnesium sulfite was allowed to react with 100% sulfur dioxide for 15 minutes at 400°; it was established that there was no dissociation of magnesium sulfite under these conditions, and the reaction products were magnesium sulfate, magnesium thiosulfate, and sulfur, which were formed in considerably greater amounts than in the decomposition of magnesium sulfite in a stream of nitrogen.

The sulfur liberated according to Equation 2-7 reacts with magnesium sulfite below 500° with the formation of thiosulfate according to the reaction

$$MgSO_3 + \tfrac{1}{2}S_2 = MgS_2O_3 \qquad (2\text{-}7)$$

Experiments conducted on the ignition of mixtures of $MgSO_3$ and sulfur in a stream of nitrogen showed that at 350°C, 8.9% of magnesium sulfite is converted to thiosulfate in 15 minutes while in the absence of sulfur, under the same conditions, 1.8% is converted.

At 550°C and above, magnesium thiosulfate is absent from the decomposition products, since under these conditions it is unstable. Consequently, the main sulfur-containing decomposition products of magnesium sulfite above 500°C in a nitrogen atmosphere are sulfur dioxide, sulfur, and magnesium sulfate.

The effect of catalysts on $MgSO_3$ decomposition was also investigated by Ketov and Pechkovskii. The presence of SiO_2 had no measurable effect on either rate or product composition. Iron and chromium oxides, however, increased the reaction rate at 500°C in a current of air. Also, higher levels of sulfate were measured in the product because of 1) enhanced direct oxidation of sulfite to sulfate, and 2) catalyzed sulfur dioxide oxidation to sulfur trioxide which subsequently reacted with available MgO formed by sulfite dissociation.

The decomposition of magnesium sulfite in a current of hydrogen resulted in formation of hydrogen sulfide according to the reaction

$$S_2 + 2H_2 \rightleftarrows 2H_2S \qquad (2\text{-}8)$$

The sulfur vapor is present due to two mechanisms, the oxidation of magnesium sulfite by sulfur dioxide (Equation 2-6) and the reduction of sulfur dioxide as shown below

$$SO_2 + 2H_2 \rightleftarrows 2H_2O + \tfrac{1}{2}S_2 \qquad (2\text{-}9)$$

The degrees of decomposition expressed as percent conversion of S after 15 minutes, in nitrogen and hydrogen were not significantly different. The addition of an iron bauxite catalyst increased the degree of decomposition at 400° - 550°C and also affected the gas phase composition, producing higher levels of sulfur and hydrogen sulfide and lower SO_2 levels. In a hydrogen atmosphere above 400°C the amount of $MgSO_4$ formed decreases because SO_2 reduction by hydrogen is more kinetically favored than reduction by $MgSO_3$. The amount of thiosulfate product is also affected by a reducing atmosphere, catalyst, and temperature as shown in Tables A2-2 and A2-3. This change is accompanied by increased levels of H_2S in the exit gases.

Kim, et al. (2-6) experimentally investigated the kinetics of $MgSO_3$ decomposition in the range 500-600°C. The effects of temperature, reaction time (2-22 minutes), and concentrations of CO_2 (0-20%), H_2O (0-20%), and O_2 (-2 to 2%) were examined. An oxygen concentration of -2% was established by addition of 1% methane to an oxygen-free atmosphere. The experiments were conducted by suspending a platinum reaction dish containing $\sim$ 300 mg of $MgSO_3$ in the reaction tube.

TABLE A2-3

TEMPERATURE DEPENDENCE OF THERMAL DECOMPOSITION OF MAGNESIUM SULPHITE, PURE AND WITH ADDITION OF 10% BAUXITE, IN A CURRENT OF HYDROGEN

Temp., °C	Pure						With Additive					
	% Conversion of S of $MgSO_3$											
	SO_2	H_2S	S_2	MgS_2O_3	$MgSO_3$	Total	SO_2	H_2S	S_2	MgS_2O_3	$MgSO_3$	TOTAL
300	0.7	0.0	2.1	2.1	5.7	10.6	0.6	0.2	2.0	2.0	5.8	10.6
350	2.1	0.4	2.5	3.8	9.0	17.8	1.8	4.3	1.5	2.4	8.2	18.2
400	5.8	1.1	3.1	4.9	10.9	25.8	3.2	23.3	1.1	0.5	9.3	38.4
450	14.8	5.9	3.1	4.0	11.3	39.1	5.1	62.1	2.8	0.0	9.1	79.1
500	33.6	15.1	3.4	0.0	10.8	62.9	17.1	44.4	23.0	0.0	7.1	91.6
550	64.2	17.5	0.3	0.0	7.5	95.5	58.0	18.4	16.3	0.0	4.9	97.6

Different temperature zones were maintained in the tube. Following equilibration at 100°C for 30 minutes with the desired gas mixture flowing at 500 cc/min, the sample was raised to the 200°C zone for 5 minutes where dehydration occurred. Then it was quickly raised to the reaction zone for the specified time, after which it was lowered to a lower-temperature zone. The product was analyzed for Mg, total S, sulfite, and reduced (thiosulfate, thionates, sulfide) sulfur. Sulfate was obtained by difference.

The results of the chemical analyses of the solid products for each run are presented in Table A2-4. The following observations were made. The extent of decomposition increased as the reaction time was increased, and the rate decreased as the reaction neared completion. The rate increased with increasing temperature over the experimental range. The decomposition was adversely affected in an oxygen atmosphere, especially at lower temperatures; a reducing atmosphere, however, failed to have a significant positive effect. The effects of H_2O and CO_2 in the atmosphere on $MgSO_3$ decomposition were small.

The kinetics of $MgSO_3$ decomposition from 500-600°C in an atmosphere of 10% CO_2, 10% H_2O, and 0% O_2 were analyzed by a least squares technique and expressed by Equations (2-10) and (2-11).

$$\frac{d\alpha}{dt} = (1-\alpha)^{3/2}\ (2.338 \times 10^{7})\ \exp\ (-37{,}000/RT)\ \text{sec}^{-1} \qquad (2\text{-}10)$$

$$2\left[\frac{1}{(1-\alpha)^{\frac{1}{2}}} - 1\right] = 2.338 \times 10^{7}\ t\ \exp\ (-37{,}000/RT) \qquad (2\text{-}11)$$

TABLE A2-4

DISSOCIATION OF MAGNESIUM SULFITE

Reaction time, min	Temp., °C	Compn. of atmosphere, %			Weight loss, %	Composition of product, %				Fraction, %, of sulfite			
							Sulfur						
		CO_2	H_2O	O_2		Mg	Total	Sulfite	Reduced	Decompd. to SO_2	Unchanged	Reduced	Oxidized to SO_4
7	526	5	5	1	46.0	25.1	21.5	15.8	0.6	35.1	47.7	1.8	15.4
17	526	5	5	-1	63.2	35.7	9.7	4.3	1.2	79.4	9.1	2.6	8.9
7	575	5	5	-1	66.4	38.3	7.1	1.7	2.8	86.0	3.4	5.5	5.2
17	575	5	5	1	62.8	35.5	10.0	1.3	1.3	78.6	2.8	2.8	15.8
7	526	15	5	-1	45.6	25.8	24.0	19.6	1.7	29.5	57.6	5.0	7.9
17	526	15	5	1	44.9	26.1	24.0	16.1	3.0	30.3	46.8	8.7	14.2
7	575	15	5	1	64.2	37.2	9.8	2.3	1.2	80.0	4.7	2.5	12.8
17	575	15	5	-1	66.1	37.5	7.1	1.4	0.9	85.7	2.8	1.8	9.7
7	526	5	15	-1	51.9	29.9	17.8	12.9	0.9	54.9	32.7	2.3	10.1
17	526	5	15	1	49.6	24.5	17.4	10.3	1.4	46.2	31.9	4.3	17.6
7	575	5	15	1	62.5	36.2	10.5	1.0	1.1	78.0	2.1	2.3	17.6
17	575	5	15	-1	64.9	37.7	8.7	1.4	2.6	82.5	2.8	5.2	9.5
7	526	15	15	1	51.2	26.3	19.2	9.9	1.4	44.7	28.5	4.0	22.8
17	526	15	15	-1	62.9	32.7	9.8	2.0	0.6	77.3	4.6	1.4	16.7
7	575	15	15	-1	64.5	35.2	9.0	2.1	1.0	80.6	4.5	2.2	12.7
17	575	15	15	1	65.4	36.7	9.7	1.0	1.0	80.0	2.1	2.1	15.9
22	550	10	10	0	67.2	37.7	6.9	1.4	0.8	86.1	2.8	1.6	9.5
2	550	10	10	0	41.0	22.7	24.5	16.4	2.0	18.2	54.8	6.7	20.4
12	602	10	10	0	68.4	40.0	4.9	0.4	1.1	90.7	0.8	2.1	6.4
12	504	10	10	0	37.6	22.5	22.1	13.4	3.1	25.5	45.2	10.5	18.9
12	550	20	10	0	63.5	33.9	10.8	2.2	0.8	75.9	4.9	1.8	17.4
12	550	0	10	0	61.0	32.0	11.3	1.5	1.2	73.2	3.6	2.8	20.4
12	550	10	20	0	49.2	25.0	17.8	0.9	0.7	46.0	2.7	2.1	49.1
12	550	10	0	0	47.0	24.2	18.7	1.2	0.8	41.4	3.8	2.5	52.3
12	550	10	10	2	55.1	28.0	15.5	1.7	0.6	58.0	4.6	1.6	35.7
12	550	10	10	-2	63.4	34.5	6.1	1.6	0.6	86.6	3.5	1.3	8.6
12	550	10	10	0	62.5	33.5	10.4	1.8	1.1	76.5	4.1	2.5	17.0
12	550	10	10	0	62.5	34.8	10.2	2.1	0.6	77.8	4.6	1.3	16.3

In these equations α is the fraction of sulfite decomposed, R is 1.987 cal/gmole °K, and T is the absolute temperature (°K). The authors state that the reaction order of 3/2 can occur when decomposition products interfere with the decomposition reaction. Extrapolation of these results indicates a reaction time of 38 seconds for 90% decomposition at 700°C or 30 seconds for 99% decomposition at 800°C. There is some doubt as to the efficiency of experimental gas-solid contact.

A mathematical model was developed for fluidized bed thermal decomposition of commercial $MgSO_3$ (2-7). The effects of coke ore gas concentration, air concentration, amount of $MgSO_3$, and bed temperature on SO_2 yield were described by a set of equations. The purpose of the investigation was to be able to specify operating parameters of a cyclic method for sinter gas desulfurization involving a boiling layer furnace to meet air pollution regulations.

Schwitzgebel and Lowell investigated the thermodynamics of the $Mg\text{-}SO_2\text{-}O_2$ and $Ca\text{-}SO_2\text{-}O$ systems (2-8). Predominance area diagrams were constructed that explain the decomposition behavior of the sulfites. Near 360°C $MgSO_3$ decomposes to $MgO + SO_2$ with side reactions yielding sulfate, thiosulfate, and elemental S as well up to 500°C. Although disproportion to $MgS + MgSO_4$ is thermodynamically feasible, this reaction does not occur because of the relatively low decomposition temperature of the sulfite, slow disproportionation kinetics below 600°C, and the stability of the thiosulfate up to 500°C.

Several additional references to thermal decomposition of magnesium sulfite appear in the literature, although the details are sketchy. In one case indirectly heating a slurry of $MgSO_3 \cdot 6H_2O$ (30%) plus $Mg(OH)_2$ (0.5%) at an unspecified temperature yielded a solid phase consisting of 50% MgO and 45% $MgSO_4$; the gas was a mixture of SO_2 and SO_3 (2-9). Ninety percent conversion of $MgSO_3 \cdot 6H_2O$ from a flue gas desulfurization system to MgO + SO_2 was achieved in an external heating rotary kiln compared to only 10-15% conversion in an internal heating rotary kiln (2-10). In a similar application a mixture of anhydrous $MgSO_3$, $MgSO_4$ and MgO is direct fired in a rotary kiln or fluidized bed, again at an unspecified temperature, to produce MgO and SO_2. The calcination is carried out in the presence of coke and carbon monoxide to reduce the sulfate to MgO + SO_2 (2-11). According to information contained in a patent, the above calcination is carried out between 750 and 1300°C (2-12). Berezina and Piraev determined by thermogravimetry that $MgSO_3$ decomposition begins at 380°C (2-13). The atmosphere was not clearly identified in the abstract.

Several patents have been issued for the recovery of elemental sulfur from $MgSO_3 \cdot 6H_2O$ generated in flue gas scrubbing. In one case the $MgSO_3 \cdot 6H_2O$ is first thermally decomposed to MgO + SO_2, the latter subsequently reduced with carbon to S, CO_2, and H_2O at 850-900°C. The reductant is added in slightly less than the chemical equivalent of SO_2 (2-10). According to a second patent description the hydrated sulfite is dried at 200-300°C (or 70-380°F) in a gas with less than 5% oxygen content and then heated with a reductant (H_2, CO, CH_4 or C) at 800-900°C producing MgO + S (2-14). A possible one-step sulfur recovery process has also been patented wherein precipitated $MgSO_3$ and $CaSO_4$ is heated at 1200°C after addition of carbon. The products are gaseous sulfur, MgO, and CaO (2-15).

2.2 Chemistry of Reduction of SO_2 to Elemental Sulfur

In this section thermodynamic, kinetic, and other pertinent information pertaining to the chemistry of obtaining elemental sulfur from sulfur dioxide is summarized. Reducing agents considered include:

- methane
- carbon monoxide
- hydrogen
- $CO + H_2$
- carbon
- coal

Each of these systems is dealt with in the following sections. The literature was searched from 1967 through the present using Chemical Abstracts. Literature reviews were relied on for access to key investigations conducted prior to 1967.

2.2.1 SO_2 Reduction by Methane

The use of methane as a reducing agent for sulfur dioxide has been developed for commercial use by Allied Chemical Corporation. A number of investigations have also been carried out by several groups of Soviet scientists. The results of the literature search for mechanistic and kinetic data relevant to the reaction between SO_2 and CH_4 are presented in Table A2-5.

TABLE A2-5

REDUCTION OF SO_2 BY METHANE

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Thermodynamic calculations up to 1200°C.	$2SO_2 + CH_4 = S_2 + CO_2 + 2H_2O$		$SO_2/CH_4 = 2$ Pressure: 1 atm Temperature: up to 1200°C	Calculation of equilibrium constants up to 1200°C and equilibrium gas mixture at 800°	High values of the equilibrium constant were calculated, indicating that the reaction will go essentially to completion. Side reactions are important. For a SO_2: CH_4 ratio of 2:1 under atmospheric pressure at 800°C the possible yield of elemental S is 68.0% (2-16).	2-16, 2-17
Kinetics of two-stage catalytic reduction.		Bauxite in both reduction steps	Gas composition - 14.7% SO_2 $SO_2/CH_4 = 2$ Space velocity 350 hr^{-1} Temperature 700-1000°C (1st reactor) 370°C (2nd reactor)	Experimental two-stage reactor	Sulfur yields were: 85% at 900°C 82% at 800°C 13% at 700°C	2-18
Thermodynamic calculations of SO_2 reduction with CH_4	$2SO_2 + CH_4 = CO_2 + S_2 + 2H_2O$		Temperature - 25-800°C CH_4 concentration - .005% SO_2 concentration - .01 %	The free energy equation for CH_4 was used: $\log K = \frac{-\Delta F^o}{4.58T}$ $- \frac{5700}{T}$ $+ 4.83 \log T$ $- 0.0016T$ $+ 2.0 \times 10^{-7}T^2$ $- 6.2$	1. The following equilibrium constants were calculated: T, °C — Log K — K 800 — 12.0 — 1×10^{12} 600 — 13.1 — 1.2×10^{13} 400 — 14.8 — 6.4×10^{14} 200 — 17.9 — 7.9×10^{17} 25 — 24.3 — 2.0×10^{24} 2. Side reactions that should be considered include: the action of H_2O on S_2 to form SO_2 and H_2S; formation of COS and CS_2.	2-19

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Thermodynamic calculations at 727 and 1000°C and kinetics of SO_2 reduction to H_2S in the 850-1000°C range	CH_4 H_2 SO_2 H_2O H_2S CS_2 CO COS CO_2 S_2 $SO_2+CH_4 = H_2S+CO+H_2O$ (1) $SO_2+CH_4 = H_2S+CO_2+H_2$ (2) $SO_2+CH_4 = COS+H_2O+H_2$ (3) $SO_2+2H_2S = \frac{3}{2}S_2+2H_2O$ (4) $\frac{4}{3}SO_2+CH_4 = \frac{2}{3}CS_2+2H_2O+\frac{1}{3}CO_2$ (5) $CS_2+2H_2S = 2S_2+CH_4$ (6) $\frac{4}{3}SO_2+CH_4 = \frac{4}{3}H_2S+\frac{2}{3}H_2O+CO_2$ (7) $SO_2+CH_4 = \frac{1}{2}S_2+CO_2+2H_2$ (8) $SO_2+CH_4 = C+\frac{1}{2}S_2+2H_2O$ (9)	Noncatalytic and in the presence of calcium sulfide	$SO_2/CH_4 = n$ $= 0.5-4$ Pressure - 1atm Temperature - 727, 1000°C Experimental temperature - 850-1000°C	Thermodynamics Calculation of equilibrium gas phase with and without excess carbon present. Experimental Catalytic flow-type reactor	1. The results of the equilibrium calculations showed that at n=2 and 727°C, the possible sulfur yield is 55.8%. At n=1 and 727 or 1000°C zero sulfur yield is predicted. 2. The rate of reduction of SO_2 by methane in the temperature range studied is controlled by the rate of pyrolysis of methane.	2-20
Thermodynamic calculations			Pressure - 1atm $SO_2/CH_4 = n$ $= 0.8-3.33$ Temperature - 627-1327°C	The calculations were based on equilibrium constants reported in the literature.	Sulfur yield is 100% when the n value is 2. At n=1 the S yield is zero at t <827°C, 3.9% at 927°C, and 60.3% at 1327°C.	2-21
Kinetics of catalytic reduction at 800-1100°C		Activated Al_2O_3	$SO_2:CH_4 = 10:6$ Temperature - 800-1100°C Catalyst particle size - 1.5-3 mm Gas flow rate	Experiments were carried out in a differential type of reactor in a 5 mm catalyst layer.	1. Kinetically the initial reaction rate is independent of the flow rate, but dependent on temperature and catalyst amount. It is a kinetic process below 950°C. 2. At higher temperatures (>950°) the reaction becomes a diffusion-kinetic process. Above 1050° it becomes a diffusion process. 3. An expression was determined to describe the kinetic phase.	2-22

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Reduction of industrial waste gas with methane over catalyst		Activated Al_2O_3	Catalyst surface area - 40-60 m^2/g Temperature - 800°-900°C Initial gas composition - 10-12% SO_2 $SO_2:CH_4$= 10:6	Consult original reference.	One m^3 of catalyst yielded 300-350 kg S/hour under experimental conditions given.	2-23
Patent description for increasing activity of catalyst at low temperatures		Activated Al_2O_3 impregnated with V_2O_5 and K_2O	Catalyst composition 95.5-97% Al_2O_3 2.0-3.0% V_2O_5 1.0-1.5% K_2O	Consult original reference.	Results were not presented in abstract.	2-24
Mechanism of catalytic reduction	$6SO_2+4CH_4=4COS+8H_2O+S_2$ Also, $COS \rightarrow CO, S_2, CO_2$, and CS_2	Quartz	SO_2/CH_4=2.2-3.4 t = 820-1135°C	Consult original reference.	Reaction shown takes place first under conditions studied. The COS then decomposes to CO and S_2, and CO_2 and CS_2. The reaction occurs on the quartz below 1050°C and in the gas phase above 1050°C. A homogeneous-heterogeneous mechanism was suggested.	2-25
Mechanism and products of catalytic SO_2 reduction	$8SO_2+6CH_4=3CS_2+S_2+2CO+CO_2+12H_2O$	Quartz	SO_2/CH_4=0.5-3.0 t = 800-950°C	Consult original reference.	In contrast to Zavadskii's results (2-25), it was reported that reduction takes place with predominant formation of CS_2 rather than COS.	2-26

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

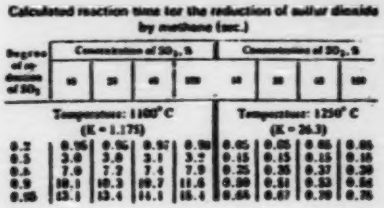
<table>
<tr><th>Scope of Investigation</th><th>Reactions and/or Species Considered</th><th>Catalyst</th><th>Parameters</th><th>Method</th><th>Results and Conclusions</th><th>Ref.</th></tr>
<tr>
<td>Thermodynamic calculations for the C-O-H-S system in the 1000-1500°K range</td>
<td>Species considered:
CH_4 CO
SO_2 H_2
S_2 COS
CO_2 CS_2
H_2O H_2S
Note: S, polyatomic S, SO molecules, and HS radicals are not stable in the temperature range considered. CS molecules may be present in significant quantities above 1027°C in the presence of excess reducing agent.
Reactions considered:
$2SO_2+CH_4=S_2+CO_2+2H_2O$ (1)
$2SO_2+4H_2S=4H_2O+3S_2$ (2)
$2H_2+S_2=2H_2S$ (3)
$CO_2+H_2=H_2O+CO$ (4)
$2CO+S_2=2COS$ (5)
$2COS=CO_2+CS_2$ (6)
Also,
$CH_4=C+2H_2$ (7)</td>
<td></td>
<td>Temperature - 727-1227°C
SO_2/CH_4 = 1.0-2.5
Pressure - 0.15-1.0atm</td>
<td>The equilibrium constants of the reactions considered were calculated based on literature equilibrium constants for dissociation of the compounds into their constituent atoms. Based on these results the equilibrium compositions were calculated for the system using ten equations, consisting of the expressions the K_e's for the 6 reactions shown plus 4 equations defining partial pressures of the system.</td>
<td>Values of log K_e
<table>
<tr><th>Reaction</th><th colspan="4">Values of log K_e at temperatures (°K)</th></tr>
<tr><th></th><th>[illegible]</th><th>[illegible]</th><th>[illegible]</th><th>[illegible]</th></tr>
<tr><td>(1)</td><td>11.8654</td><td>11.2987</td><td>10.7258</td><td>10.2563</td></tr>
<tr><td>(2)</td><td>1.5720</td><td>1.9701</td><td>2.6338</td><td>3.0634</td></tr>
<tr><td>(3)</td><td>4.2687</td><td>3.4146</td><td>2.0012</td><td>1.1368</td></tr>
<tr><td>(4)</td><td>−0.1543</td><td>0.0085</td><td>0.2183</td><td>0.4164</td></tr>
<tr><td>(5)</td><td>1.6407</td><td>0.7528</td><td>−0.8078</td><td>−1.5844</td></tr>
<tr><td>(6)</td><td>−0.8481</td><td>−0.8262</td><td>−0.7954</td><td>−0.7728</td></tr>
</table>
Results were also presented in tabular form for the compositions of equilibrium mixtures, sulfur distribution, and heats of reaction for the SO_2-CH_4 system considered. Dependence of the equilibrium yields of SO_2, S_{elem}, H_2S, COS, and CS_2 on temperature SO_2:CH_4 ratios, and pressure were presented graphically.
In general, the yield of elemental S was maximized at an SO_2/CH_4 ratio of 2.0. Sulfur yield also increased with increasing temperature over the range investigated for ratios lower than 2.0.</td>
<td>2-27</td>
</tr>
<tr>
<td>Kinetics of thermal reduction of concentrated SO_2 gases by methane</td>
<td>Main reaction:
$2SO_2+CH_4=S_2+CO_2+2H_2O$ (1)
Intermediate and side reactions:
$CH_4=C+2H_2$ (2)
$CH_4+H_2O=CO+3H_2$ (3)
$2SO_2+2C=S_2+2CO_2$ (4)
$2SO_2+4H_2=S_2+4H_2O$ (5)
$2SO_2+4CO=S_2+4CO_2$ (6)
$2CO+S_2=2COS$ (7)
$C+S_2=CS_2$ (8)
$2H_2+S_2=2H_2S$ (9)
(Cont.)</td>
<td></td>
<td>Temperature- 900-1250°C
Reaction Time- .23-14.4 sec
Gas Feed Rate- 2.4 liters hr^{-1}
SO_2 content of SO_2 containing gas-100% and 10-40%
Reducing gas composition: 95-99% CH_4 Balance: hydrocarbons
SO_2/CH_4=1.3-2.2</td>
<td>Experiments were conducted in quartz flow-type reactors in which the reaction zone was delimited by two inserts formed by sealed quartz tubes.</td>
<td>SO_2/CH_4=1.9 and 100% SO_2 gas
1. The overall SO_2 conversion and S yield were strongly temperature dependent:
<table>
<tr><th>t, °C</th><th>Overall SO_2 Conversion, %</th><th>S yield %</th><th>Reaction Time, sec</th></tr>
<tr><td>900</td><td>83</td><td>45</td><td>14.4</td></tr>
<tr><td>1100</td><td>94</td><td>81</td><td>3</td></tr>
<tr><td>1250</td><td>94</td><td>81</td><td>1.4</td></tr>
</table>
2. The experimental S yield was slightly higher than the equilibrium yield at 1100-1250°C after 0.78-0.34 sec.
(Cont.)</td>
<td>2-28</td>
</tr>
</table>

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
	$2SO_2+1.5CH_4=2H_2S+1.5CO_2+H_2O$ (10)				3. At 900°C the reduction is slow.	
	$2SO_2+1.5CH_4=CS_2+0.5\ CO_2+3H_2O$ (11)				SO_2/CH_4=1.27 and 100% SO_2 Gas	
					1. Overall SO_2 conversion and H_2S yield were strongly temperature-dependent; see Reactions (10) and (11).	
					2. The rate of reduction is significantly higher than at SO_2/CH_4 ratio of 1:9, but the elemental S yield is low.	
					SO_2/CH_4=2.0 and Lower SO_2 Gas	
					1. Overall SO_2 conversion is 80-95% for reaction times of 0.34-12.9 seconds.	
					2. The elemental S yield is 15-20% abs. less than SO_2 conversion, and H_2S yield is 10-20%.	
					SO_2/CH_4=1.3-1.45 and Lower SO_2 Gas	
					1. SO_2 conversions were 100%, and S yields were 50±10%.	
					Kinetics	
					1. Satisfactory agreement was found between experimental and predicted values based on the assumption that the rate is controlled by the rate of methane pyrolysis up to 1250°C. Results are tabulated below.	

(Cont.)

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)



Calculated reaction time for the reduction of sulfur dioxide by methane (sec.)

Degree of reduction of SO_2	Concentration of SO_2, %				Concentration of SO_2, %			
	10	20	40	100	10	20	40	100
	Temperature: 1100°C (K = 1.175)				Temperature: 1250°C (K = 26.3)			
0.2	0.95	0.96	0.97	0.98	0.05	0.05	0.05	0.05
0.5	3.0	3.0	3.1	3.?	0.15	0.15	0.15	0.16
0.8	7.0	7.2	7.4	7.9	0.25	0.26	0.27	0.29
0.9	10.1	10.3	10.7	11.6	0.30	0.31	0.32	0.34
0.95	13.1	13.4	14.1	15.4	0.65	0.67	0.70	0.76

2. The reaction time is expressed as:

$$t=\frac{1}{K}\left[(1+0.3N)\ln\frac{1}{1-x} - 0.3Nx\right]$$

where: x = degree of CH_4 decomposition

N = fraction of (SO_2+CH_4) in initial mixture.

3. If H_2S is the main by-product, a higher rate is measured. A different mechanism is probably responsible.

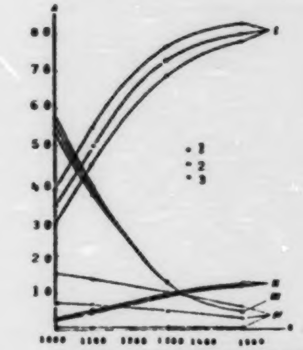
Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Economics and process descriptions for SO_2 reduction to S for high temperature (~1250°) and catalytic low temperature (~800°) processes applied to non-ferrous sulfide roaster gases.		Dunite Mugay Bauxite High Clay Bauxite Gypsum Alunite Active Clay	SO_2 Content of Gases - 6-100% Temperature - Catalytic 750-900 Noncatalytic 1250°C SO_2/CH_4 ratio- 1.3-2.0 Pressure - 1 atm Catalyst contact times - 0.07-0.97 sec.	Consult original reference.	1. Noncatalytic Tests - The degree of SO_2 reduction increased with temperature and SO_2/CH_4 ratio. The following products were formed at SO_2/CH_4=2.0, 1227°C, and 1 atm: S 70.4% COS 0.7 CS_2 0.0 H_2S 12.8 SO_2 12.1 2. Catalytic Process - Catalyst efficiencies were determined at various conditions listed to the left. Activity increased in the following order at 900°C: dunite, Mugay bauxite, high-clay bauxite, gypsum, alunite, active clay. Different orders were observed at 800 and 850°C. Products were: H_2S, COS, CS_2, and S.	2-29 2-30

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Thermodynamic calculations for SO_2 reduction by CH_4 in presence of carbon and carbon + steam	Reactions (1)-(6) in Ref. 2-27 $CH_4 = C_{(gr)} + 2H_2$ (7) $C_{(gr)} + SO_2 = CO_2 + 0.5S_2$ (8) $C_{(gr)} + S_2 = CS_2$ (9)		Temperature - 727-1227°C Pressure - 0.15-1.0 atm SO_2/H_2O - 6,12,100 SO_2/CH_4 - 1.0,2.5	Calculations were based on constants reported in the literature. Methods used were similar to those reported in Ref. 2-27.	1. The equilibrium constants for Reactions (7)-(9) are shown below:	2-31

Reaction No. (1)	Values of log K_p at temperatures (°K)			
	[illegible]	[illegible]	[illegible]	[illegible]
7	0.9923	1.4215	2.0004	2.3426
8	5.6198	5.4628	5.2482	5.0250
9	1.0023	0.600	0.4043	0.3220

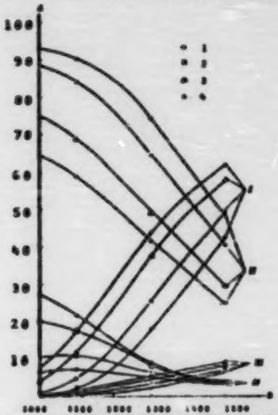
2. Equilibrium compositions, sulfur distributions, and heats of reactions for the SO_2-CH_4-H_2O-C and SO_2-CH_4-C systems were tabulated. Sulfur distributions in the first system as a function of temperature, pressure, SO_2/H_2O and SO_2/CH_4 ratios are shown graphically below.



Dependence of the equilibrium distribution of sulfur between the components on temperature and the $SO_2:H_2O$ ratio at $\Sigma p_1 = 1$ atm in reduction of SO_2 by carbon. A) Yield (%); B) temperature (°K). $SO_2:H_2O$ ratio: 1) 6; 2) 12; 3) 100. Sulfur components: I) CS_2; II) S_2; III) COS; IV) H_2S.

(Cont.)

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
					 Dependence of the equilibrium distribution of sulfur between the components on temperature and the $SO_2:CH_4$ ratio at $\Sigma p_i = 1$ atm in reduction of SO_2 by carbon and methane. A) Yield (%); B) temperature (°K). $SO_2:CH_4$ ratio: 1) 1.0; 2) 1.33; 3) 2.0; 4) 2.5. Sulfur components: I) CS_2; II) H_2S; III) S_2; (V) COS. 3. Although the thermodynamics of elemental S production do not seem favorable, industrial coke plants for S production are feasible since they operate under non-equilibrium conditions.	
Laboratory investigation of SO_2 reduction by natural gas under catalytic and non-catalytic conditions.		Bauxite Reduced Alunite	Temperature - 700-1100°C Gas Flow Rate - 12-70 ml/min Catalyst effect Number of Stages - 1,2	Quartz Tube Reactor	1. The sulfur yield was less than 40% in an uncatalyzed system. 2. The catalytic system was strongly temperature dependent. The S yield with bauxite as catalyst increased from 28.1 to 83.3% with temperature increase from 800 to 1000°, then decreased to 78% with further increase to 1100°. With reduced alunite an increase in yield of 15.6 to 81.8% was measured over the range 700 to 1100°.	2-32

(Cont.)

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
					3. Increase in gas flow decreased sulfur yields except for the case of the bauxite-catalyzed system at 1000-1100°. 4. Best results (98-99%S yields) were achieved with two-stage reduction under the following conditions: 1st stage - 900° reduced alunite; 2nd. stage - 370° bauxite; SO_2/CH_4 =2.0; gas flow 10-13 ml/min.	
Optimization study of catalytic reduction of SO_2		Bauxite	Temperature - 900°C Flow Rate - 900-1000 hr^{-1} Catalyst Layer Height - 50 mm (1st. stage) 23 mm (2nd. stage) Catalyst particle size - 0.5-1.0 mm	Fluidized bed catalytic reactor	Sulfur yields in one- and two-stage processes, respectively, were 84% and 92%.	2-33
Optimization study of catalytic reduction of SO_2		Bauxite	SO_2 content - 5-30% Bed temperature Space velocity Number of stages	Fluidized bed catalytic reactor	Optimum temperatures for all SO_2 compositions were 900° for first stage and 250° for the second stage. The optimum space velocities depended on the SO_2 content: 5% SO_2 460 hr^{-1} 14% SO_2 534 hr^{-1} 30% SO_2 755 hr^{-1} Total sulfur yields were 70-75% for one stage and 95-96% for two stages.	2-34

TABLE A2-5 - REDUCTION OF SO_2 BY METHANE (cont.)

Scope of Investigation	Reactions and/or Species Considered		Catalyst	Parameters	Method	Results and Conclusions	Ref.
Literature review and thermodynamic calculations for SO_2 reduction by methane	Main Reactions:			Temperature-527-1527°C		The equilibrium constants for reactions (1) and (2) were calculated from 527 to 1527°C. Based on the results, both reactions go essentially to completion above 1127-1227°C as can be seen in the table below.	2-35
	$2SO_2+CH_4=S_2+CO_2+2H_2O$	(1)					
	$4SO_2+3CH_4=4H_2S+3CO_2+2H_2O$	(2)					
	Possible Side Reactions:						
	$2SO_2+2CS_2=3S_2+2CO_2$	(3)					
	$SO_2+3H_2=H_2S+2H_2O$	(4)					
	$CH_4+2S_2=CS_2+2H_2S$	(5)					
	$SO_2+2H_2=2H_2O+\frac{1}{2}S_2$	(6)					
	$CS_2+2H_2O=2H_2S+CO_2$	(7)					
	$SO_2+2COS=2CO_2+\frac{3}{2}S_2$	(8)					
	$CH_4+3CO_2=4CO+2H_2O$	(9)					
	$CH_4+H_2O=CO+3H_2$	(10)					
	$CH_4+2H_2O=4H_2+CO_2$	(11)					
	$SO_2+2CO=2CO_2+H_2O$	(12)					
	$COS+H_2O=H_2S+CO_2$	(13)					
	$H_2+\frac{1}{2}S_2=H_2S$	(14)					
	$CO+H_2O=CO_2+H_2$	(15)					
	$2COS=CO_2+CS_2$	(16)					
	$2H_2O+\frac{3}{2}S_2=2H_2S+SO_2$	(17)					
	$CO+\frac{1}{2}S_2=COS$	(18)					

Temperature			Log Kp *		Kp	
°K	°C	°F	Reaction(1)	Reaction(2)	Reaction(1)	Reaction(2)
800	526.84	980.31	12.612	37.618	4.09×10^{12}	4.15×10^{37}
900	626.84	1160.31	12.065	35.289	1.16×10^{12}	1.94×10^{35}
1000	726.84	1340.31	11.625	33.421	4.22×10^{11}	2.64×10^{33}
1100	826.84	1520.31	11.260	31.888	1.82×10^{11}	7.73×10^{31}
1200	926.84	1700.31	10.956	30.616	9.04×10^{10}	4.13×10^{30}
1300	1026.84	1880.31	10.691	29.525	4.91×10^{10}	3.35×10^{29}
1400	1126.84	2060.31	10.463	28.593	2.90×10^{10}	3.92×10^{28}
1500	1226.84	2240.31	10.263	27.779	1.83×10^{10}	6.01×10^{27}
1600	1326.84	2420.31	10.085	27.065	1.22×10^{10}	1.16×10^{27}
1700	1426.84	2600.31	9.929	26.437	8.49×10^{9}	2.73×10^{26}
1800	1526.84	2780.31	9.785	25.873	6.10×10^{9}	7.46×10^{25}

* Data for each molecular species from JANAF tables

Calculations of equilibrium compositions for various feeds show that the product mixture contains no unreacted methane, neglibible CS_2, and only small amounts of COS. The balance was elemental S (S_2,S_6,S_8) H_2S, CO_2, C, CO, H_2O, H_2. Comparison of the results with literature data show that equilibrium can be achieved using high temperature, low to moderate space velocities, and/or good catalysts (activated alumina, silica gel, activated bauxite, or Allied's proprietary catalyst as opposed to quartz). Formation of carbon can be avoided with active catalysts, or by high temperature noncatalytic conditions, assuming space velocities which are not too high.

Equilibrium constants for several other reactions related to reduction of SO_2 with CH_4 were also calculated and plotted as a function of temperature (Exhibit 11-2 in original ref.).

2.2.2 Reduction of Sulfur Dioxide by Carbon Monoxide

The reduction of SO_2 by carbon monoxide has been the subject of numerous investigations. The stoichiometry of the main reaction was established in 1885 (2-36)

$$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2 \qquad (2\text{-}12)$$

In the absence of a catalyst the reaction is slow; therefore the emphasis of many studies of SO_2 reduction by CO is on catalysis. Table A2-6 summarizes the reuslts of the literature survey on chemistry of SO_2-CO systems.

TABLE A2-6

SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE

<table>
<tr><th>Scope of Investigation</th><th>Reaction and/or Species Considered</th><th>Catalyst</th><th>Parameters</th><th>Method</th><th>Results and Conclusions</th><th>Ref.</th></tr>
<tr>
<td>Thermodynamic investigation of SO_2 reduction systems based on published thermodynamic data.</td>
<td>$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2$ (1)
$CO + \frac{1}{2}S_2 = COS$ (2)
$COS = \frac{1}{2}CO_2 + \frac{1}{2}CS_2$ (3)
$S_2 = \frac{1}{3}S_6 = \frac{1}{4}S_8$ (4)</td>
<td></td>
<td>Temperature:
350-1200°C</td>
<td>Log K and K for reaction (1) were calculated from the free energy equation in the range 350-1200°C.</td>
<td>1. Reaction (1) Calculations:
<table>
<tr><th>t, °C</th><th>K</th></tr>
<tr><td>350</td><td>7.59×10^{12}</td></tr>
<tr><td>500</td><td>1.95×10^{9}</td></tr>
<tr><td>600</td><td>3.98×10^{7}</td></tr>
<tr><td>700</td><td>1.74×10^{6}</td></tr>
<tr><td>800</td><td>1.35×10^{5}</td></tr>
<tr><td>1000</td><td>2.29×10^{3}</td></tr>
<tr><td>1200</td><td>2.00×10^{2}</td></tr>
</table>
Similar calculations were performed for Reactions (2) and (3).

2. In a gas mixture of 2:1 CO/SO_2 (or excess SO_2), the amount of CS_2 formed will be negligible. Thus, Reaction (3) was not considered in further calculations.

3. The following gas composition was calculated considering Reactions (1) and (2).

TABLE IV. PERCENTAGE GAS COMPOSITION AT TOTAL EQUILIBRIUM SULFUR CONVERSION
<table>
<tr><th>Temp., °C.</th><th>% CO_2</th><th>% CO</th><th>% COS</th><th>% SO_2</th><th>% S Conversion</th></tr>
<tr><td>1200</td><td>75.2</td><td>16.2</td><td>0.33</td><td>8.27</td><td>90.5</td></tr>
<tr><td>1000</td><td>87.0</td><td>7.0</td><td>0.80</td><td>4.20</td><td>94.5</td></tr>
<tr><td>800</td><td>95.6</td><td>2.0</td><td>1.00</td><td>1.40</td><td>95.5</td></tr>
<tr><td>700</td><td>97.8</td><td>0.7</td><td>0.80</td><td>0.70</td><td>96.5</td></tr>
<tr><td>600</td><td>98.5</td><td>0.2</td><td>0.80</td><td>0.30</td><td>98.8</td></tr>
<tr><td>500</td><td>99.4</td><td>0.02</td><td>0.40</td><td>0.20</td><td>99.4</td></tr>
<tr><td>350</td><td>99.94</td><td><0.01</td><td>0.04</td><td>0.02</td><td></td></tr>
</table>
4. In the presence of carbon, continuous reduction of SO_2 by CO takes place. Section 2.2.6 deals with this chemical system.</td>
<td>2-19</td>
</tr>
<tr>
<td>Experimental investigation of thermodynamics of Reaction (1) in 1000-1500°C.</td>
<td>$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2$</td>
<td></td>
<td>Temperature:
Exp.: 1000-1200°C
Extrapolated: 1500°C

25 vol.% CO and SO_2 in feed.</td>
<td>Consult original reference.</td>
<td>Equilibrium constants were experimentally determined at 1000 and 1200°C. Additional constants were calculated up to 1500°C.</td>
<td>2-37</td>
</tr>
</table>

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Experimental study of catalytic kinetics of SO_2 reduction.	$SO_2 + 2CO = 2CO_2 + \frac{1}{2}S_2$ (1) $CO + \frac{1}{2}S_2 = COS$ (2) $2COS + SO_2 = 2CO_2 + \frac{3}{2}S_2$ (3)	Pyrrhotite (FeS_2) Boehmite (hydrated and acid-soluble forms of alumina) Guiana bauxite (lightly calcined) Activated alumina	Catalyst Temperature: 250-800°C. Reactant Mixture: 63% CO 35% SO_2 CO generated from coke Contact time: 60 sec.	Quartz tube reactor.	1. The uncatalyzed reaction proceeds slowly even at 800°C. Pyrrhotite is an efficient catalyst at 700°C. At lower temperatures alumina in slightly hydrated and acid-soluble forms (boehmite) was efficient. Bauxite and activated alumina were also satisfactory catalysts. 2. The mechanism probably involves formation of surface compounds of sulfur dioxide and the catalyst. 3. In the 300-600°C range the reduction is apparently first order. The temperature coefficient Rd ln k/d (1/T) varied from 14,000 kg-cal (bauxite) to 18,000 kg-cal (pyrrhotite). 4. The heats of reaction are: Reaction — ΔH (1) $51,760 - 2.75\ T + 0.0028\ T^3$ (2) 22,500 kg-cal (3) $6760 - 2.75\ T + 0.0028\ T^2$ 5. The most efficient application is to use CO (or COS) as SO_2 reductant as a step subsequent to reduction by carbon. Optimum conversion to elemental sulfur of 96% is predicted based on 97% catalyst efficiency and 0.994 denoting the conversion at equilibrium at 500°C.	2-38
Thermodynamics of the SO_2-CO system with respect to combustion systems.	SO_2, CO, CO_2, SO, S_2, O, O_2, S.		Initial Reactant Mixtures: (1) 4% SO_2 - 4% CO (2) 1% SO_2 - 1% CO Temperature: 1000-2500°K	Calculations based on JANAF data.	1. The character of the equilibrium curves is determined by the ratio of reactants rather than their absolute concentration. 2. The species listed to the left were generated. The species O, O_2, and S are abundant at the higher temperatures. 3. The S_2 mole fraction shows little change as SO_2 varies from 1 to 4%.	2-39

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Experimental study of catalytic kinetics of SO_2 reduction.	$2CO + SO_2 = \frac{1}{2}S_2 + 2CO_2$ $CO + \frac{1}{2}S_2 = COS$ $2COS + SO_2 = \frac{3}{2}S_2 + 2CO_2$ $COS = \frac{1}{2}CO_2 + \frac{1}{2}CS_2$ Proposed Reactions with Transition Metal Catalyst: $\frac{1}{x}S_x + \frac{1}{2}M = \frac{1}{2}MS_2$ $yCO + M = M(CO)y$ $M(CO)y + \frac{1}{2}MS_2 = \frac{1}{2}M + M(CO)_{y-1} + SCO$ $CO + \frac{1}{2}MS_2 = \frac{1}{2}MS + SCO$ $2SCO + SO_2 = \frac{3}{x}S_x + 2CO_2$	Iron Alumina Mixed Iron/Alumina Mixed Iron/Silica Mixed Iron Silicate/ Alumina Red Bauxite Surinam Red Mud Commercial Catalysts: Commercial alumina catalysts containing transition metals Ca_2SiO_4 + Co Graphite + Zn, Cu Zeolite Clay Silica Gel Iron Oxide Diatomaceous Earth Corundum Laboratory-prepared transition metal oxide-alumina pellets	Catalyst composition Pellet size Temperature (350-600°C) Partial pressures of SO_2, CO, CO_2, O_2.	Single-pass vertical fixed-bed catalytic flow reactor.	1. In absence of a catalyst the rate was extremely slow even at 950°C. 2. With pure iron or pure alumina present, SO_2 conversion was immeasurable at 500°C. 3. Mixed iron/alumina catalysts result in significant conversion of SO_2 at low temperatures and low concentrations of SO_2 (usually 0-5%) and CO. Other transition metal/alumina catalysts also were effective. Synergistic effect explained by a possible dual-site mechanism. Mixed iron/silica catalysts were not effective. 4. Pellet size inversely affected reaction rate for diameters greater than 1 mm. 5. At 350°C a measurable reaction rate was observed with 41.2% iron, the rate doubled approximately every 50° interval in the range investigated. 6. The apparent activation energy was 18.3 Kcal per mole. 7. The initial reaction rate was independent of SO_2 partial pressure but was directly proportional to the CO partial pressure; formation of COS was also directly related to the CO partial pressure, maximizing at 400°C. CO_2 concentrations less than 15% did not affect the rate, but O_2 levels greater than 0.5% caused considerable rate reduction. 8. Less COS was formed in the presence of an Al_2O_3-containing catalyst than with Fe or Fe/SiO_2 materials. The COS was an intermediate formed on the Fe (or other metal) sites. It begins to form when all the iron surface is sulfidized (i.e., converted to FeS), with an apparent decrease in activity. The intermediate migrates to Al_2O_3 if available where it reacts with chemisorbed SO_2 to produce elemental S and CO_2. 9. Red bauxite and Surinam red mud showed promise as commercial catalysts for recovery of S from waste gases. 10. Alumina catalysts were found to be activated by sulfur and deactivated by pretreatment with HF. This was explained by application of Bronsted vs. Lewis acid site sorption mechanism.	2-40 2-41 2-42 2-43 2-44 2-45 2-46 2-47 2-48 2-49

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Experimental investigation of catalytic conversion of SO_2 by CO	**Main Reactions:** $2CO + SO_2 = \frac{1}{2}S_2 + 2CO_2$ $CO + \frac{1}{2}S_2 = COS$ $CO + \frac{1}{2}O_2 = CO_2$ **Side Reactions:** $2COS + SO_2 = \frac{3}{2}S_2 + 2CO_2$ $COS + \frac{3}{2}O_2 = CO_2 + SO_2$ **Possible Reactions if H_2O Present:** $H_2O + CO = H_2 + CO_2$ $3H_2 + SO_2 = H_2S + 2H_2O$ $2H_2 + S_2 = 2H_2S$ $2H_2S + SO_2 = 2H_2O + S_2$ $COS + H_2 = CO + H_2S$ $COS + H_2O = CO_2 + H_2S$ **Additional S Equilibria** $S_2 = S_x$ ($x = 3,4,5,6,7,8$)	**Screened:** Copper on alumina*, cupric oxide on alumina, silver on alumina, molybdenum trioxide on silica, alumina. * Selected to investigate further because it was only one to exhibit sustained activity toward SO_2-CO reaction.	SO_2/CO ratios Pressure - ∿ 1 atm Temperature catalyst Catalyst	Flow reactor operating isothermally and near atmospheric pressure in the absence of oxygen and water.	1. Temperatures greater than 390°C are required to achieve 90% conversion of SO_2, even at high CO levels. [Gas composition was in flue gas concentration range.] 2. At CO ratios >1 and temperatures > 430°C reduction occurs rapidly; e.g., contact time of 0.22 seconds. [Note - CO ratio defined as $(N_{CO} - 2N_{O_2})/N_{SO_2}$ where N_{CO}, N_{O_2}, and N_{SO_2} are upstream concentrations of CO, O_2, and SO_2, respectively.] However, in the range >430 to 525°C and for >0.1 second contact time, 30% of sulfur compounds formed are other than elemental sulfur, mostly COS. To overcome this, two possible approaches exist. a. Operate at temperatures >815°C where thermodynamics of COS formation are unfavorable. This option was not considered further. b. Operate under conditions favorable to reaction of COS and SO_2. [Catalytic kinetics are higher at 540°C than for COS-CO reaction.] Possibly operate with two beds; in first (480°C) convert all SO_2 in two-thirds of gas stream to COS and in second reactor (315°C) COS would react with SO_2 in remainder of feed stream to produce $S + CO_2$. Up to 97% conversion of SO_2 was achieved for contact times as low as 0.18 seconds. Catalyst activity remained constant over a continuous 30-hour run.	2-50 2-51 2-52
Experimental study of kinetics of SO_2 reduction over a copper on alumina catalyst.	[Same as above.]	8% copper on alumina (Harshaw Cu 0803)	**Inlet gas composition:** 2000 ppm SO_2 3500-6500 ppm CO 14% CO_2 Balance N_2 **Length of runs:** few - 45 hours **Contact time:** 0.230 seconds (cont.)	Fixed catalyst bed in a tubular flow reactor.	1. The kinetics of the reduction of SO_2 by CO can be adequately correlated by a first order model for predicting the dependence of SO_2 conversion on process variables. The equation below was derived for prediction of k_{SO_2} where k_{SO_2} represents the catalyst activity expressed as $k_{SO_2} = \frac{-\ln(1-X_{SO_2})}{\theta}$ $\ln k_{SO_2} = A'' - \frac{E}{R}\frac{1}{T} + B$ (CO ratio 1.4) (cont.)	2-53

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Experimental study of kinetics of SO_2 reduction over a copper on alumina catalyst. (cont.)			Space velocity: 15,000 hr^{-1} Temperature: 382-440°C CO ratio $= \frac{ppm\ CO}{2(ppm\ SO_2)}$ $= 0.9\text{-}1.6$ (The effects of water, oxygen, and nitric oxide were not studied.)		where: X_{SO_2} = fractional conversion of inlet SO_2 concentration θ = contact time, based on reactor inlet conditions and total catalyst volume, sec. $A'' = 19.8$ B (at 732°F) = 1.53 B (at 795°F) = 1.07 E/R = 2.16×10^4°R 2. The COS yield can be directly predicted from SO_2 conversion for a range of temperatures, CO ratios, and contact times. 3. It was concluded that a single catalytic bed can remove no more than 75-80% of inlet SO_2 as elemental sulfur.	
Investigation of the effect of water on catalytic SO_2 reduction.	[Same as above.]	8% copper on alumina.	Inlet gas composition: 2000 ppm SO_2 – % CO (see CO ratio) 3.4% O_2 14% CO_2 0-9.6% H_2O Balance N_2 CO Ratio: 1.43-1.51 at 440°C 1.35-1.37 at 493°C Space velocity: 29,300-38,700 hr^{-1}	Fixed catalytic bed in a tubular flow reactor.	1. Based on thermodynamic calculations, at a given temperature higher CO ratios are required in the presence of water to convert a percentage of the feed SO_2. H_2S production is favored by the presence of water (compared to COS in a dry system), lower temperatures, and higher CO ratios. Hydrogen formation increases with increasing CO ratio at a given temperature, but decreases with decreasing temperature at a given CO ratio. The water-gas shift reaction is thermodynamically favored, with resultant H_2 reacting with sulfur to produce H_2S. 2. Based on experimental results, neither H_2 nor H_2S was detected. Thus, the water-gas shift reaction did not proceed under the test conditions. The water reduced the activity of the catalyst and greatly reduced COS formation. The catalyst poisoning appeared to be reversible.	2-54

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Simultaneous removal of SO_2 and NO by reduction with CO	$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2$ $CO + \frac{1}{2}S_2 = COS$ $CO + NO = CO_2 + \frac{1}{2}N_2$ $2COS + SO_2 = \frac{3}{2}S_2 + 2CO_2$	Copper on alumina Silver on alumina Palladium on alumina Manganese on silica gel Silver on silica gel Copper on silica gel Ruthenium on alumina Iron on alumina Chromium on alumina Iron/chromium/alumina	Simulated flue gas Composition (2-57): 2000 ppm SO_2 ~6000 ppm CO 0-1000 ppm NO 14% CO_2 Balance N_2 Temperature: 440°C Space velocities: $\sim 10^4$ hr^{-1} Catalysts	Fixed catalyst bed in vertical tubular flow reactor.	1. Metals on alumina were the most active catalysts for reduction of SO_2 alone. Copper on alumina was tested extensively. 2. Simultaneous reduction of NO and SO_2 by catalyzed reaction with CO is possible. Thermodynamic calculations showed that optimum initial ratio of CO to SO_2 is slightly less than 2 to minimize COS formation. Essentially complete reduction of NO_x is possible. 3. The copper-alumina catalyst was less active for the combined reduction than for either (i.e., NO or SO_2) separately. 4. Maximum SO_2 conversion (to either COS or S) is limited to 75-80% in a one-bed process. 5. The Cu-, Fe-, and Cr-alumina catalysts were all active in the combination reduction, but an iron/chromium/alumina catalyst was ten times as active.	2-55 2-56 2-57 2-58
Laboratory investigation of dual-bed catalytic reduction of simulated flue gas.	$CO + NO = CO_2 + \frac{1}{2}N_2$ $2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2$ $CO + \frac{1}{2}S_2 = COS$ $2COS + SO_2 = \frac{3}{2}S_2 + 2CO_2$	Iron-chromia in first bed. Activated alumina in second bed.	Bed temperature: 630-700°F Composition of inlet gas to second bed (i.e., ratio of COS to SO_2)	Vertical tubular flow reactor containing two successive catalyst beds.	The dual-bed concept was successful in achieving 90% conversion of SO_2 in simulated flue gas to sulfur at temperatures <370°C and high space velocities (at least 20,000 hr^{-1} on the combined bed). Proper COS to SO_2 ratio entering the second bed (stoichiometric ratio of 2) can be effected by controlling the catalyst bed temperature.	2-56
Optimization study for catalytic reduction of SO_2 in one- and two-stage processes.		Aluminum oxide	Number of beds Bed height Gas flow rate Catalyst particle size Temperature	Fluidized catalyst bed reactor.	The optimum parameters were: 600°C; flow rate - 365-570 hr^{-1}; bed height: first stage - 65-70 mm, second stage - 20 mm; catalyst particle size - 0.25-0.50 mm. The sulfur yield in the one-stage process was 90-1% and 94% in the two-stage reactor.	2-59
Mechanistic study of catalytic reduction of SO_2	$SO_2 + 2CO = 2CO_2 + S_x$	Aluminum oxide	Reaction time: 40-320 sec.	Flow reactor with catalyst deposited in thin layer on walls. (cont.)	1. Reaction rate becomes appreciable at 450°C and above. Retardation results with SO_2 increase, while CO increase causes faster velocity. 2. At initial SO_2:CO ratio of 1:3 and 600°C, 30% conversion of reactants was measured. (cont.)	2-60

TABLE A2-6 - SULFUR DIOXIDE REDUCTION BY CARBON MONOXIDE (cont.)

Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Mechanistic study of catalytic reduction of SO_2 (cont.)				Chromatographic analysis of initial, intermediate, and final components: CO, SO_2, CO_2, COS, but not S. ESR spectrum of SO radical.	3. The SO radical was detected in the heterogeneous-homogeneous reduction of SO_2.	
Experimental study of catalytic reduction of SO_2	Refer to Table 6 in original reference.	13 catalysts including: $Cu-Al_2O_3$ (various ratios) $Cu-Cr_2O_3$ $Fe-Al_2O_3$ $Fe-Cr_2O_3$ $Co-Al_2O_3$ $Ni-Al_2O_3$ $Cu-Cr_2O_3-Al_2O_3$ $Cu-Fe-Al_2O_3$ $Cu-Cr_2O_3-Al_2O_3$	Reaction temperature: 300-550°C Inlet gas composition: 2% SO_2 4-8% CO 0-3.2% O_2 0-6.6% H_2O Balance N_2	Flow-type reactor with a fixed catalyst bed.	1. In the absence of H_2O and O_2, the copper on alumina catalysts were superior. Reduction in Cu content led to reduced amounts of COS. 2. In the presence of H_2O and O_2, the following were observed: . temporary catalyst poisoning by water vapor; . catalysts readily deactivate due to structural changes - possibly formation of sulfides or sulfates; . possibility of side reactions (none actually proved).	2-61
Thermodynamics and kinetics of catalytic SO_2 reduction by CO in the system $SO_2-CO-CO_2-N_2$ for SO_2 removal from combustion furnace exhaust.	$SO_2 + 2CO = \frac{1}{2}S_2 + 2CO_2$	Activated alumina Alumina + iron Alumina + silver Alumina + copper Alumina + calcium Alumina + magnesium Bauxite	Temperature: 100-900°C Contact time: 0.02-0.30 sec SO_2 Concentration: 0.17-0.19% CO concentration: 0.4-1.6% CO_2 concentration: 0-15% Gas flow rate: 0.25-1.5 $\ell\text{-min}^{-1}$ Amount of catalyst: 0-20 cm^3 Space velocity: 1000-3000 hr^{-1}	Fixed-floor apparatus consisting of vertical quartz reaction tube and gas mixing apparatus.	1. The maximum conversion of SO_2 was obtained at 400-500°C using bauxite as a catalyst. 2. The catalysts containing oxides of metals such as Fe, Cu, Ca, and Ag in each alumina were highly active. 3. The equilibrium conversion of SO_2 increased with increasing temperature and CO concentration, and decreased with increasing CO_2 concentration. 4. The reaction rate in the presence of bauxite had first order dependence with respect to SO_2 and CO concentrations, but was adversely affected by CO_2 above 600°C.	2-62

2.2.3 Reduction of Sulfur Dioxide with Hydrogen

An early explanation of the reduction of sulfur dioxide by hydrogen is shown below (2-19).

$$SO_2 + 2H_2 \rightleftharpoons 2H_2O_{(g)} + \tfrac{1}{2}S_2 \qquad (2\text{-}13)$$

$$H_2 + \tfrac{1}{2}S_2 \rightleftharpoons H_2S \qquad (2\text{-}14)$$

$$2H_2O_{(g)} + \tfrac{3}{2}S_2 = 2H_2S + SO_2 \qquad (2\text{-}15)$$

The author assumed S_2, S_6, and S_8 to be the vapor phase sulfur species, although a later worker presented evidence for the S_3, S_4, S_5, and S_7 molecules as well (2-63). The equilibrium constants for reactions (2-13), (2-14), and (2-15) were calculated from 300-1100°C based on free energies (K_1, K_2, and K_3, respectively). These are summarized in Table A2-7. The calculated equilibrium ratio of $S:H_2S$ was approximately four at 325°C assuming an initial mixture of two moles of water and one-half mole of S_2.

Inclusion of all the gas phase sulfur species in the model leads to eight independent reactions describing the system (2-64). The reactions and the respective equilibrium constant equations are shown in Table A2-8. Murdock and Atwood computed the equilibrium compositions and sulfur yields over the temperature range 300-1100°C and at several nonstoichiometric feed compositions in the presence of nitrogen diluent. Formation of elemental sulfur was favored at lower temperatures although significant quantities of hydrogen sulfide were predicted even at low temperatures. The results are shown graphically in Figure A2-6. Calculations of thermodynamic equilibrium conversions of hydrogen and sulfur dioxide, and hydrogen sulfide and sulfur yields at various feed compositions

TABLE A2-7

EQUILIBRIUM CONSTANTS FOR THE SYSTEM SO_2-H_2S-H_2O-H_2-S_2

Temp., °C.	Log K_1	K_1	Log K_2	K_2	Log K_3	K_3
1100	3.53	3.4×10^3	0.87	7.4	−1.77	1.10×10^{-2}
900	4.51	3.2×10^4	1.47	29.5	−1.57	2.69×10^{-2}
700	5.85	7.1×10^5	2.28	191	−1.29	5.13×10^{-2}
500	7.82	6.6×10^7	3.49	3.1×10^3	−0.84	1.45×10^{-1}
300	11.10	1.3×10^{11}	5.60	4.0×10^5	0.00	1.0
113	...	......	...	.....	1.30	20.0

TABLE A2-8

EQUATIONS USED TO CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE REACTIONS IN THE $SO_2/S_4/H_2/H_2S/H_2O$ SYSTEM AT DIFFERENT TEMPERATURES

Reaction		Equilibrium constant (*T* in °K)*	Reference
2	$1\frac{1}{2}S_2 \rightleftharpoons S_3$	$K_1 = \exp(13.3 - 0.0188T)/RT$	Detry, *et al.* (1967)
3	$2S_2 \rightleftharpoons S_4$	$K_2 = \exp(28.2 - 0.0367T)/RT$	Detry, *et al.* (1967)
4	$2\frac{1}{2}S_2 \rightleftharpoons S_5$	$K_3 = \exp(47.8 - 0.0557T)/RT$	Detry, *et al.* (1967)
5	$3S_2 \rightleftharpoons S_6$	$K_4 = \exp(66.3 - 0.0751T)RT$	Detry, *et al.* (1967)
6	$3\frac{1}{2}S_2 \rightleftharpoons S_7$	$K_5 = \exp(78.9 - 0.0893T)/RT$	Detry, *et al.* (1967)
7	$4S_2 \rightleftharpoons S_8$	$K_6 = \exp(96.8 - 0.1103T)/RT$	Detry, *et al.* (1967)
8	$H_2O + \frac{1}{2}S_2 \rightleftharpoons H_2 + \frac{1}{2}SO_2$	$K_7 = \exp(-7944/T - 0.5066 \ln T + 1.75 + 1.525 \times 10^{-3}T - 2.648 \times 10^{-7}T^2)$	Doumani, *et al.* (1944)
9	$H_2 + \frac{1}{2}S_2 \rightleftharpoons H_2S$	$K_8 = \exp(19.4 - 0.00771\, T \ln T + 1.30 \times 10^{-6}T^2 + 0.0125T)$	Kelley (1937)

* *R* is 0.0019869 kcal/g mol °K.

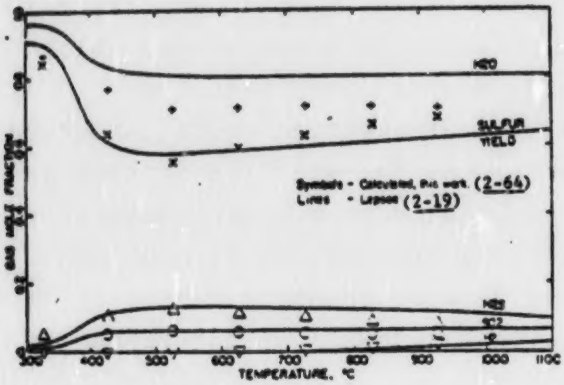


FIGURE A2-6 - EQUILIBRIUM GAS COMPOSITION FOR THE REDUCTION OF SULFUR DIOXIDE WITH HYDROGEN AT 760 mm Hg PRESSURE: □, H_2 (MURDOCK. 1973); O, SO_2; △, H_2S; +, H_2O; x, SULFUR YIELD; -, LEPSOE (1938).

as presented in Table A2-9 indicated that sulfur dioxide concentration should be maximized in order to achieve the highest sulfur yields. Increasing temperature over the range 345 to 390°C was found to have a negative effect on sulfur yield. Thermodynamically, almost complete conversion of sulfur dioxide is possible at temperatures below 400°C.

Kinetic investigations were conducted to define the reaction mechanism and to determine if hydrogen sulfide formation could be suppressed to further increase sulfur yields (2-64). The effects of catalyst to feed ratio, flow rates, and temperature were studied in the presence of an activated bauxite catalyst. Significant levels of conversion of SO_2 to elemental sulfur were observed at reaction temperatures in the 300-400°C range. The rate of the primary reaction route (Equation 2-13) was found to be independent of the sulfur dioxide concentration and first order with respect to the hydrogen concentration, expressed as:

$$r_{SO_2} = -\tfrac{1}{2} k_{H_2} P_{H_2}$$

where:

k_{H_2} = 0.014 ± 0.001 mol-hr^{-1} (g of cat.)$^{-1}$ atm^{-1} at 375°C

The rate of H_2S formation can be expressed as

$$r_{H_2S} = k_{H_2S} \frac{P_{H_2}^{3/2}}{P_{SO_2}^{1/2}}$$

where:

k_{H_2S} = 2.9x10^{-4} ± 0.3x10^{-4} mole-hr^{-1} (g of cat.)$^{-1}$ atm^{-1} at the same temperature.

TABLE A2-9

THERMODYNAMIC EQUILIBRIUM CONVERSIONS OF HYDROGEN AND SULFUR DIOXIDE AND THE YIELD OF HYDROGEN SULFIDE FOR THE $H_2/SO_2/S_x/H_2S/H_2O/N_2$ SYSTEM AT 375°C and 1 ATM

Feed composition, mole %		% Conversion		Product	
				Mole fraction	Ratio
H_2	SO_2	H_2	SO_2	H_2S	$S_1:H_2S$
2.67	1.33	100.0	90.1	2.73×10^{-3}	3.38
5.33	1.33	74.9	100.0	1.33×10^{-2}	5.18×10^{-7}
8.0	1.33	49.9	100.0	1.33×10^{-2}	5.79×10^{-9}
2.67	2.67	100.0	48.2	9.51×10^{-4}	12.5
5.33	2.67	100.0	90.7	4.67×10^{-3}	3.98
8.0	2.67	99.9	100.0	2.65×10^{-2}	5.81×10^{-8}
2.67	4.0	100.0	32.5	7.07×10^{-4}	17.4
5.33	4.0	100.0	63.8	2.22×10^{-3}	10.5
8.0	4.0	100.0	91.4	6.90×10^{-3}	4.3

Rate expressions for the other species were also derived. Comparison of experimental and calculated SO_2 conversions agreed well over the entire range, 0 to 98% conversion; however, the predicted yields of hydrogen sulfide were lower than experimental yields for w/N_o values above 11.8 (w = grams of catalyst, N_o = moles/hr of feed). The temperature dependencies of the overall rate constants, k_{H_2} and k_{H_2S}, were experimentally determined and correlated using the Arrhenius equation.

A reaction mechanism was proposed which was shown to be consistent with observed initial kinetics. The mechanism involved oxidation, reduction, desorption, and regeneration of sulfur sites.

Non-catalytic reduction of sulfur dioxide reduction by hydrogen was investigated at 700-900°C in a quartz tube reactor (2-65). Sulfur yield increased from zero to 20.7% over this range. The initial gas composition was 10 ml SO_2, 10 ml O_2, 80 ml N_2, and 50 ml H_2. The sulfur yields improved significantly in the presence of bauxite catalyst. At 800°C and 160 ml/min flow rate the yields were 56 and 86% respectively for a one- and two-step reduction. The catalyst also prevented the formation of hydrogen sulfide below 900°C; this is compared to a 12% yield at 800°C in uncatalyzed tests. Additional catalysts were later studied at lower temperatures (2-66). The best sulfur yield obtained was 98-100% over reduced alunite at 600°C and 54-90 ml/min gas flow rate.

Shakhtakhtinskii and co-workers (2-67) reported that near complete conversion of SO_2 was possible by hydrogen at 600°C in a steel reactor in contrast to the results obtained with the quartz reactor described above. Preheating the SO_2 and H_2 separately to 350°C made much lower reactor temperatures feasible (300°C) without a loss in sulfur yield.

2.2.4 Reduction of Sulfur Dioxide with CO + H_2

Shakhtakhtinskii and co-workers have reported a number of studies of SO_2 reduction by converted natural gas. Catalyzed and non-catalyzed experiments were conducted. Information contained in Chemical Abstracts since 1967 is summarized in Table A2-10. No data on kinetics or mechanisms were available.

2.2.5 Sulfur Dioxide Reduction by Coal

One reference to the reduction of SO_2 with coal was found in the recent literature. This gas purification process involves reaction of the humidified gas with coal at temperatures $\geq$ 425°C (2-75). A high sulfur content coal may be used. No additional information was available in the abstract of this patent.

TABLE A2-10

REDUCTION OF SO_2 WITH CO + H_2

Reactant Gas Description	Experimental Conditions				S Yield (%)	Remarks	Ref.
	No. of Stages	Catalyst	Temperature (°C)	Space Velocity (hr^{-1})			
Roaster gas - SO_2 content not specified. Reformed natural gas - chiefly H_2 and CO. Reducing gas: roaster gas volume ratio = 2:1	Two	Reduced alunite in first stage; bauxite in second stage.	800	Not given in abstract.	Not given in abstract.		2-68
Reducing gas:							
H_2- 71.20-73.52%	One	Al_2O_3	600	See remarks.	87	S yield decreased at higher temperatures because of increased H_2S formation.	2-69
CO - 22.72-26.40%	One	Bauxite	600		≤ 78		
CH_4 - 0.80-3.10%	One	Bauxite	800		82		
SO_2 gas - composition not described in abstract.	Two	Al_2O_3	450-700		97	Optimal conditions:	
	Two	Bauxite	450-700		97	. Space velocity - 630-740 hr^{-1} . Catalyst bed depth - 60-80 mm	
14 and 20% SO_2 gas mixtures.	Two	Bauxite (fluidized bed)	400 (1st stage)	434 (14% SO_2 gas)	97-98		2-70
Converted natural gas.			200-350 (2nd stage)	461 (20% SO_2 gas)			
7 and 20% SO_2 gas mixtures Converted natural gas with 5-20% residual CH_4.	Experimental technique was not described in abstract.				Not given in abstract.	Sulfur yield decreased with increased residual CH_4 levels and increased with increasing temperatures.	2-71
75% SO_2 gas	(Not clearly specified in abstract.)	Bauxite (fluidized bed)	450-500		<85		2-72
Converted natural gas.			500-700		85		
			>700		80-81		
	One	Bauxite	500	1040-2075	86		
			500	>2075	<86		
			600-700	2270	Optimal		

TABLE A2-10 - REDUCTION OF SO_2 WITH CO + H_2 (cont.)

Gas Composition	Experimental Conditions				S Yield (%)	Remarks	Ref.
	No. of Stages	Catalyst	Temperature (°C)	Space Velocity (hr^{-1})			
75% SO_2 gas Converted natural gas (cont.)	Two	Bauxite	250-450	Not given in abstract.	96-97 (S yield from reaction in Remarks; Overall S yield not given.)	The following reaction occurs in 2-stage catalysis in this temperature range: $2H_2S + SO_2 \rightarrow 1.5\ S_2 + 2H_2O$	
SO_2 gas - composition not described in abstract. Converted natural gas.	One	Steel reactor	800 (optimum)	Not given in abstract.	"Most"	Gas flow rate: 0.0004 m/sec	2-73
			400		96-97	Operation at lower temperature possible with preheating of initial gases to 400°C.	
50-100% SO_2 gas mixture. Converted natural gas	One	Al_2O_3 (fluidized bed)	450-600	1100	Not given in abstract.		2-74
	One	Natural bauxite	450	1100	Not given in abstract.		
	Two	Bauxite	450-500 (1st stage) 450 (2nd stage)	1120	Not given in abstract.		

2.2.6 Sulfur Dioxide Reduction by Carbon

Studies of the reduction of SO_2 by various forms of carbon have been reported in the literature. These studies are summarized in Table A2-11. Mechanisms have been suggested involving formation of carbon-sulfur and carbon-oxygen bonds. Lepsoe (2-19) reported that in the presence of carbon, continuous reduction of SO_2 takes place through the following reaction scheme:

$$2CO + SO_2 = 2CO_2 + \frac{1}{2}S_2 \qquad (2\text{-}16)$$

$$CO_2 + C = 2CO \qquad (2\text{-}17)$$

$$SO_2 + C = CO_2 + \frac{1}{2}S_2 \qquad (2\text{-}18)$$

Thus the chemistry of this system is related to that discussed in Section 2.2.2.

TABLE A2-11

REDUCTION OF SO_2 BY CARBON

Reducing Agent	Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Carbon (coke)	Kinetics of SO_2 reduction by C, CO, and COS.	$SO_2 + C = CO_2 + \frac{1}{2}S_2$ (1) $CO_2 + C = 2CO$ (2) $SO_2 + 2CO = 2CO_2 + \frac{1}{2}S_2$ (3)		Temperature: 850-1200°C Contact time: 1.5-22.0 min	Vertical quartz reaction tube.	An expression for the rate of CO_2 formation between 900 and 1200°C was derived: $(CO_2) = 1.1[(SO_2)^{0.1} - (SO_2)]$ where ( ) denotes moles in the reaction product. Above 1200°C the rate of SO_2 reduction was apparently diffusion controlled.	2-38
Carbon	Study of carbon-oxygen system.				Consult original reference.	The rate of reaction (2) above is insignificant at temperatures of 250-300°C, even up to 700°C. Therefore this mechanism cannot explain CO formation observed (2-38).	2-76
Coke	Investigation of kinetics and mechanism of SO_2 reduction by coke under conditions similar to copper smelting	CO, CO_2, SO_2, CS_2, COS		10 and 100% coke in reduction layer. Gas-coke contact time: ∿ 2 sec Reactor temperature: Initial - 1300°C Final - 900°C	Analyzed gas product composition in apparatus simulating conditions of sulfide ore smelting.	Under the conditions tested 78-80% reduction of SO_2 was measured. Product analysis was not reported in the abstract.	2-77
Charcoal and Coke	Experimental investigation of SO_2 reduction to S and CS_2				Integral flow reactor with a fixed charcoal or coke bed.	An induction period of about three hours was observed before conversion of SO_2 to CS_2. Elemental sulfur also was produced.	2-78
Medium Activated Coconut Shell Charcoal	Experimental study of chemisorption of SO_2 by and regeneration of active carbon to determine mechanism and effects of temperature and CO.	$SO_2 + C = CO_2 + \frac{1}{2}S_2$ (1) $CO_2 + C = 2CO$ (2) $SO_2 + 2CO = 2CO_2 + \frac{1}{2}S_2$ (3)		Sorption temperature: 50-650°C Regeneration at higher temperatures (typically 950°C for 90 min in He flow) Effect of CO in inlet gas (2%) Gas flow: 200 cm^3/min Effective linear flow: 153 cm/min (cont.)	Packed bed flow reactor.	1. Between 50 and 300°C, the following observations were made. In the absence of oxygen and water, carbon has limited SO_2 sorption capacity. Chemisorption occurs on only 1% of BET surface area, and is independent of temperature in this range. Physical adsorption decreases from 3% to 0.3% between 50 and 150°C and is negligible above 250°C. Analysis of regeneration effluent indicated that regeneration of charcoal after sorption in the lower range (50-300°C) occurs through (cont.)	2-79

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

Reducing Agent	Scope of Investigation	Reactions and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Medium Activated Coconut Shell Charcoal (cont.)				Average residence time: 3.5 sec Inlet gas composition: 0.5% SO_2 in He		reduction of chemisorbed SO_2 to elemental sulfur. Results are tabulated below. 2. Catalyst thermal regeneration was accompanied by weight loss attributed to carbon conversion to oxides, especially at temperatures >500°C. 3. At 650°C the reduction between SO_2 and carbon took place rapidly, yielding CO, CO_2, and S. Significant amounts of S left the bed and condensed in cooler parts, leaving active sites for further SO_2 reduction. 4. The presence of CO in the inlet gas had an inhibiting effect on oxygen complex formation on the carbon surface. At 550°C evidence for reaction (3) was found, but at lower temperatures, e.g., 350°C, extensive formation of COS occurred. Results are shown below.	

MATERIAL BALANCES ON REACTION SYSTEMS SO_2-C AND SO_2-CO-C

	Gaseous reactants, moles × 10^{-6}/min		Time product sample taken	Gaseous products, moles × 10^{-6}/min			
Temp. (°C)	SO_2	CO	Min	SO_2	CO	CO_2	COS
650	4.5	nil	420	nil	1.0	3.8	nil
600	4.5	nil	130	nil	0.5	1.8	nil
550	4.5	17.0	15	0.4	8.9	8.6	0.2
550	4.5	17.0	195	0.4	8.2	7.7	0.4
500	4.5	17.0	240	nil	6.6	10.6	1.2
350	4.5	17.0	330	nil	4.6	9.6	3.4

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

Reducing Agent	Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
1. Medium Activated Coconut Shell Charcoal 2. Bituminous Coal Char	Experimental investigation of simulated flue gas and carbon between 500 and 800°C.	Side Reactions: $H_2S + CO = COS + H_2$ (1) $H_2S + CO_2 = COS + H_2O$ (2) Mass spectrometer analyzed exit gases for CO_2, H_2S, CO, COS, SO_2, H_2, H_2O, and He.		Run time: 350-500 min Temperature: 500-800°C Carbon forms Inlet gas composition: 0.35% SO_2 2.3% H_2O 15.8% CO_2 3.2% O_2 Balance helium	Quartz fixed-bed, flow tube system using simulated flue gas. Gas products analyzed by mass spectrometry.	1. With the coconut shell charcoal at 600 and 800°C the exit gas was free of S compounds for a certain period of time, which was longer at the higher temperature. Then H_2S and COS broke through in both cases, although their profiles were quite different. An explanation for this phenomenon was based on increasing reaction rate between carbon with H_2S and COS with increasing temperature. 2. In the bed itself a C-S surface complex was formed. This complex has a high thermal stability. 3. While the sulfur content of the bed at H_2S-COS break-through was 3.4 times higher at 800 than 600°C, the residence time of the gas in bed at breakthrough decreased by 40% going from 600 to 800. 4. SO_2 did not appear in the exit gas until 200 min at 500°C and 500 min at 700°C. At 800°C, S retention on the bed exceeds at least 11% before SO_2 break-through occurs. 5. Reactions (1) and (2) were shown to account for the observed H_2S:COS ratios during the experiment. 6. The results of the bituminous coal char reaction were more complex. Consult original article for details. 7. Carbon was found to be a poorer catalyst for oxidation of COS to elemental S than for H_2S oxidation. 8. When the exit gas of the reduction reactor (containing slight excess O_2) was passed through a second carbon reactor at 100°C, no sulfur compound was measured in the effluent even after four hours, indicating that conversion of COS and H_2S to S was occurring.	2-80

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

Reducing Agent	Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Wood Charcoal Pellets	Thermogravimetric study of kinetics of catalytic and noncatalytic reduction of SO_2 on charcoal in range 615-940°C.		Na_2CO_3	Temperature: 615-940°C SO_2 feed concentration Catalyst	Thermogravimetric apparatus consisting of chainomatic analytical balance and tubular furnace.	1. No single controlling step was found for controlling the reaction under all experimental conditions. However, a prominent influence by chemical reaction was shown. An integral rate equation, assuming chemical reaction control, was proposed: $r_o d_o f = A \exp(-E/RT) P_{SO_2}^{0.69} t$ where: r_o = initial radius of pellet d_o = density of pellet f = fractional thickness of pellet (related to fractional conversion of carbon) A = frequency factor E = activation energy T = temperature P_{SO_2} = partial pressure of SO_2 t = time 2. Values of A and E were determined: Noncatalytic: $A = 104 \text{ g cm}^{-2} \text{ min}^{-1}$ $E = 19{,}870 \text{ cal mol}^{-1}$ Catalytic: $A = 1.12 \text{ g cm}^{-2} \text{ min}^{-1}$ $E = 10{,}200 \text{ cal mol}^{-1}$	2-81
Coke	Parametric study of SO_2 reduction over hot carbon surface, with emphasis on CS_2 yield.		Na_2CO_3	Bed temperature: 920 and 1000°C Catalyst concentration: Particle size - 8-11 British sieve standard. Pretreatment of coke. Reaction time: 200 min. SO_2 concentration: 72%.	Not described in abstract.	The CS_2 yield increased with: . increasing bed temperature, . in presence of catalyst, . decreasing particle size, . coke pretreatment, . increased reaction time.	2-82

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

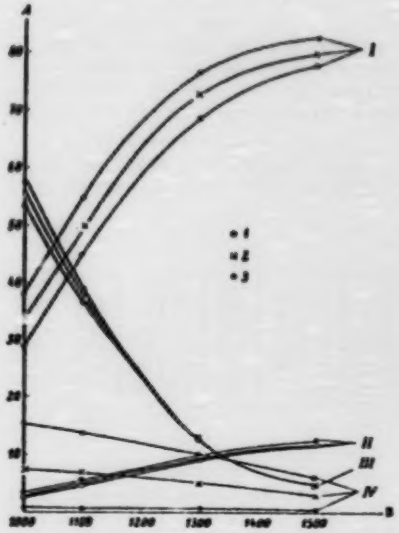
Reducing Agent	Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Carbon	Thermodynamic calculations of SO_2 reduction by carbon in presence of H_2O in range 727-1227°C, emphasizing CS_2 yield.	Overall reaction at 1300-1500°K: $5C + 2SO_2 = CS_2 + 4CO$		Temperature: 727-1227°C SO_2:H_2O ratio: 6-100 Pressure: 0.15-1.0 atm	Thermodynamic calculations based on method described in Reference 2-27.	1. Equilibrium yield of CS_2 was greatest (70-80%) at 1027-1227°C. 2. The distribution of sulfur between components in the equilibrium mixture at 1 atm is shown below.  Dependence of the equilibrium distribution of sulfur between the components on temperature and the SO_2:H_2O ratio at $\Sigma p_i = 1$ atm in reduction of SO_2 by carbon. A) Yield (%); B) temperature (°K). SO_2:H_2O ratio: 1) 6; 2) 12; 3) 100. Sulfur components: I) CS_2; II) S_2; III) COS; IV) H_2S. 3. Equilibrium yields of elemental sulfur and H_2S were low.	2-31
Carbon (several commercial samples)	Kinetics of reaction system C-SO_2.			Influence of components of ash: SiO_2 Al_2O_3 MgO CaO Fe_2O_3	Pulsation reaction chromatography in a microreactor. Combination of thermogravimetry and gas chromatography to investigate solid phase in relation to ash composition.	Results were not described in abstract.	2-83

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

Reducing Agent	Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Carbon	Thermodynamics of $C-SO_2$ system.	Reaction products considered: CO CO_2 COS CS_2 S_2		Temperature: 527-1227°C Effect of N_2, CO_2, O_2, H_2O.	Calculations based on minimization of free energy of the system.	1. Equilibrium composition of the base reaction mixture ($C-SO_2$) was calculated. 2. The equilibrium composition of a simulated waste gas was presented. Removal of SO_2 as elemental S was judged thermodynamically feasible. 3. The presence of H_2O is highly undesirable because of H_2S formation.	2-84
Metallurgical Coke and Coal Char	Define chemistry of SO_2 reduction by carbon at temperatures near 1200°C and space velocities of 700-800.			Temperature: ~1200-1760°C Space velocities: 700-800 hr^{-1} Inlet gas - SO_2 in N_2	DTA TGA Fixed and fluidized bed reactors.	1. In the fixed bed reactor the following results were reported:	2-85

Input gas flow, ft³/min	GHSV	Input, %		Avg. temp., °F	Output, %				Test lgth., min.
		SO_2	N_2		CO_2	N_2	CO	COS	
0.86........	191	100	..	2210	<1	4	80	7	15
3.0........	391	100	..	2100 2220	<1	5	76	7	25
0.9........	315	100	..	2230	6	1	68	22	25
1.9........	813	13	81	2600 2100	<1	80	18	1	60

Formation of COS may be avoided by quenching the reaction to prevent interaction of CO and S.

2. The results from the fluidized bed are shown below. Pure SO_2 feed gas was used in this series. A dilute SO_2 stream (13%) yielded reduced quantities of COS.

Input gas flow, ft³/hr	GHSV*	Input, % SO_2	Avg. temp., °F	Output, %				Test length, min.
				CO_2	N_2	CO	COS	
6.80........	773	13	2230	5	77	18	....	60
4.354........	812	100	2100	32.5	..	43.0	34.5	30
4.384........	778	100	2220	11.0	..	42.0	47.0	60

$$\text{* Gaseous hourly space velocity} = \frac{\text{Ft}^3\ \text{gas/hr @ 60F}}{\text{Ft}^3\ \text{bed (initial)}}$$

(Cont.)

TABLE A2-11 - REDUCTION OF SO_2 BY CARBON (cont.)

Reducing Agent	Scope of Investigation	Reaction and/or Species Considered	Catalyst	Parameters	Method	Results and Conclusions	Ref.
Metallurgical Coke and Coal Char (cont.)						3. The reaction was heat balanced with addition of air to SO_2 stream and substitution of coal char for metallurgical coke. 4. The results of rate studies showed that 50% of the graphite is reacted within 15 minutes at 1260°C. Faster rates were observed with char than with graphite. The kinetics are highly temperature dependent.	
Low Volatile Char	Experimental investigation of SO_2-carbon system at 800-950°C.	$2C + 2SO_2 = 2CO_2 + S_2$ (1) $C + S_2 + CO_2 = 2COS$ (2) $C + 2COS = CS_2 + 2CO$ (3) $C + CO_2 = 2CO$ (4) $C + S_2 = CS_2$ (5)		Feed gas - 10% SO_2 in N_2. Feed gas flow rate: 40-120 ml/min Temperature: 800-950°C Carbon mass: 4 and 10 g Reactor pressure: 1 atm	Vitreous silica flow reactor in tube furnace. Effluent gas analyzed for SO_2, CO_2, CO, CS_2, COS. Elemental S obtained by difference.	1. The set of equations shown to the left describes the kinetically effective stoichiometry occurring. 2. The two reactions yielding CS_2 are similarly temperature-dependent in the range 800-950°C. 3. Reaction (5) is more temperature-dependent than (3). 4. A mechanistic argument was proposed to remove the redundancies in the kinetics of the proposed stoichiometric scheme where CS_2 was involved. 5. Reliable rate constants could not be estimated based on the data.	2-86

2.3 Conversion of Hydrogen Sulfide to Elemental Sulfur

The presence of excess hydrogen in the reducing atmosphere for SO_2 reduction will result in H_2S formation, especially at high temperatures. For this reason the chemistry involved in conversion of H_2S to elemental sulfur is of interest in this program. The majority of processes available for accomplishing this are based on the Claus reaction. Originally developed as a gas phase process, many modifications have been developed. In this section the chemistry of the gas phase reactions will be discussed, and a brief summary of modifications in aqueous and organic media will be presented. Miscellaneous routes for conversion of H_2S to elemental sulfur will also be briefly addressed.

2.3.1 Gas Phase Claus Process

This section contains a summary of the variations of the gas phase Claus process: the straight-through process, the split flow process, and the direct oxidation process. The three variations have been widely used to treat acid gas streams having H_2S concentrations ranging from 15 to 100% H_2S. The Sulfreen process, which is a low temperature modification of the basic Claus process used in treating Claus tail gases, is also covered.

The Claus process was designed for streams containing H_2S and CO_2. The main reactions involve partial oxidation of the hydrogen sulfide to sulfur dioxide with subsequent conversion of remaining H_2S and SO_2 yielding elemental sulfur as shown below.

$$H_2S + {}^3\!/_2 O_2 = SO_2 + H_2O \qquad (2\text{-}19)$$

$$2H_2S + SO_2 = \frac{3}{j} S_j + 2H_2O \qquad (2\text{-}20)$$

The overall Claus reaction may be written as:

$$H_2S + \tfrac{1}{2}O_2 = \frac{1}{j} S_j + H_2O \qquad (2\text{-}21)$$

The first detailed study of the reaction equilibria between H_2S and air was based on a stoichiometric O_2/H_2S ratio (i.e., 0.5) in the initial mixture at total pressures of 0.5, 1, and 2 atm (2-87). The compounds assumed to be present in the equilibrium mixture included S_2, S_6, S_8, H_2O, H_2S, SO_2, and N_2. In a later study these results were verified; also, the influence of hydrocarbons and CO_2 in the starting mixture was pointed out (2-88).

Basing calculations on more recently determined equilibrium constants and considering additional compounds (S_4, H_2, O_2, H_2S_2, SO, and SO_3) in the equilibrium mixture, similar sulfur yields at 550-650°K were predicted (2-89). The calculated levels of the new compounds added were found to be very low. Similar conclusions were reached in a different study for temperatures in the 400 to 1750°K range (2-90).

Bennett and Meisen (2-91) calculated equilibrium compositions of mixtures resulting from reactions between H_2S and air at atmospheric pressure over the range 600-2000°K (327-1727°C). The O_2/H_2S ratio ranged from 0.05-1.0. These parameters were chosen in order to simulate Claus furnace conditions. Compared to earlier studies additional species were considered, particularly nitrogen compounds and free radicals, the latter being potentially important at high furnace temperatures. In this study CO_2, COS, CS_2, NH_3, and hydrocarbons were omitted.

The technique used consisted of calculating equilibrium constants for each possible reaction at 100°K intervals based on free energy data. Partial pressures of the "key components," S_2, H_2S, H_2O, and N_2, were guessed from which the partial pressures of the remaining species could be determined by applying the law of mass action to their formation reactions. The total partial pressures, and the atomic ratios of unbound oxygen to sulfur, hydrogen to sulfur, nitrogen to oxygen, and carbon to sulfur were subsequently evaluated. Using an iterative procedure, these were made to converge, yielding characterization of equilibrium composition. The results of the calculations showed that 25 compounds were present in concentrations >0.1 ppm for at least some temperatures in the 600-2000°K range. Optimum sulfur yields were predicted at O_2/H_2S ratios of less than 0.5 (stoichiometric) since this suppressed further oxidation of elemental sulfur.

More recently equilibrium studies were performed in which all Claus reactions were considered by the same researchers (2-92, 2-93). The following assumptions were made:

1. All compounds behave as ideal gases,
2. Initial acid gas contains only H_2S, CO_2, and H_2O,
3. Air consists entirely of nitrogen (79%) and oxygen (21%),
4. Total pressure of the system is one atmosphere.

Equilibrium compositions were calculated for mixtures resulting from reactions among H_2S, CO_2, H_2O, and air at atmospheric pressure over the range 600-2000°K (327-1727°C). The amount of air was varied from 20-300% of the stoichiometric amount based on Reaction 2-21. The acid gas composition included up to 10% H_2O and up to 30% CO_2. In addition to the reactions already presented in the above discussions, the following were considered:

$$H_2O + \tfrac{1}{2}S_2 = \tfrac{1}{2}O_2 + H_2S \qquad (2\text{-}22)$$

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad (2\text{-}23)$$

$$CO_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 = HCN + O_2 \qquad (2\text{-}24)$$

$$2HCN = C_2N_2 + H_2 \qquad (2\text{-}25)$$

$$CO_2 + 2H_2S = CS_2 + 2H_2O \qquad (2\text{-}26)$$

$$2CS_2 + H_2 = C_2H_2 + 2S_2 \qquad (2\text{-}27)$$

$$\tfrac{1}{2}C_2H_2 + \tfrac{3}{2}H_2 = CH_4 \qquad (2\text{-}28)$$

$$C_2H_2 + H_2 = C_2H_4 \qquad (2\text{-}29)$$

$$C_2H_4 + \tfrac{1}{2}O_2 = C_2H_4O \qquad (2\text{-}30)$$

$$CO_2 = CO + \tfrac{1}{2}O_2 \qquad (2\text{-}31)$$

$$CO_2 + H_2S = COS + H_2O \qquad (2\text{-}32)$$

$$COS + H_2 = CS + H_2O \qquad (2\text{-}33)$$

The same calculation technique used in the previous study (2-91) was employed.

Of the 36 compounds considered, all except HCN, C_2N_2, CH_4, C_2H_2, C_2H_4, and C_2H_4O had partial pressures greater than 10^{-7} atmospheres for at least some temperature in the temperature range investigated. The partial pressures of the remaining 30 compounds were plotted as a function of temperature. Sulfur yields were shown as functions of temperature, CO_2 partial pressure, and O_2 partial pressure. In order to predict actual Claus furnace compositions, the effect of adiabatic conditions was also examined. Preheating of the feed gases was recommended in order to achieve high sulfur yields possible with less than stoichiometric amounts of air.

Another thermodynamic investigation of Claus combustion chambers was performed by Neumann (2-94). A thermodynamic model modified by semiquantitative considerations from reaction kinetics was employed to calculate equilibrium compositions from waste gases containing H_2S and SO_2. Other species in the feed that were considered included S_2, H_2O, N_2, H_2, and/or CO_2.

Catalytic effects on oxidation of H_2S by oxygen have been the subject of numerous studies in recent years. Oxidation on active coals gave 100% S yields compared to ~50% SO_x yield on "treated" coals (2-95). The catalytic properties of the active coals were related to surface carbon oxides, free radicals, and adsorbed cations. No further details were available in the abstract. Bauxite, synthetic zeolite, and other catalysts were tested in a low-temperature, two-stage system (2-96). The pre-heated gas (350-460°C) was mixed with a stoichiometric amount of air before passing through the first reactor, cooled to 160°C to condense S, reheated to 260-270°C, and passed through the second reactor. Overall H_2S conversion was ~90% with S the main product.

Larin and Erofeeva reported that the heat of the exothermic reaction

$$2H_2S + O_2 = 2H_2O + S_2 \qquad (2\text{-}21)$$

was 106 kcal (2-97). The reaction was carried out in a fluidized bed packed with activated carbon.

Reaction kinetics and activation energies associated with H_2S oxidation by molecular oxygen over various catalysts have been reported over the range 130-200°C (2-98). Catalytic mechanisms for active C, molecular sieve 13X, and liquid sulfur were discussed. Cariaso also studied the oxidation over porous carbons (2-99), while others investigated the catalytic effectiveness of cobalt molybdate and related materials at H_2S levels below 4000 ppm (2-100). Bauxite catalysts of hydroargillite structure were found to be effective for conversion of COS resulting during production of S from H_2S-containing gases in the presence of CO_2 (2-101).

Numerous investigations of the reaction between H_2S and SO_2 to produce water and elemental sulfur (Equation 2-20) have been conducted. Mechanisms and kinetics of the alumina-catalyzed reaction were determined using infrared spectroscopic techniques (2-102). The relative rate constants for the reactions below were 75:1:5 at 250°C in the presence of a commercial cobalt-molybdate catalyst (2-103).

$$SO_2 + 2H_2S = 2H_2O + \frac{3}{x} S_x \qquad (2\text{-}20)$$

$$SO_2 + 2COS = 2CO_2 + \frac{3}{x} S_x \qquad (2\text{-}34)$$

$$COS + H_2O = CO_2 + H_2S \qquad (2\text{-}35)$$

The H_2S-SO_2 reaction appeared to be diffusion controlled with an activation energy of 5.5 kcal/mole. Georgiev studied the effect of steam concentration on the reaction (2-104).

An induction period τ for the Claus reaction was measured by Kokochashvili and Labadze (2-105). The reactant mixture composition and the state of the reactor walls were shown to have an effect on the duration of τ. Coating of the walls with Cr oxide had a decreasing effect, while coating with MgO, CuO, and MnO_2 completely eliminated the induction period. Adversely, treatment with KCl or $K_2B_4O_7$ inhibited the reaction.

There are three basic arrangements of the gas phase Claus process: straight-through, split stream, and direct oxidation. The main features of each are summarized below. The Sulfreen process based on low-temperature gas phase reaction is also described here.

Straight-Through Process

The straight-through process generally gives the highest overall recovery of the three variations of the Claus process. It also allows maximum heat recovery at a high temperature level.

In the straight-through process, the acid feed gas is mixed with a stoichiometric quantity of air, determined from Equation 2-21.

The combined stream is introduced to a furnace where combustion occurs at about 2500°F. H_2S is converted to elemental sulfur to the extent of 30% to 69% (2-106).

The remainder of the H_2S is converted to SO_2, COS, and CS_2 by the following reactions:

$$CH_4 + 4S \rightleftharpoons CS_2 + 2H_2S \tag{2-36}$$

$$CO_2 + H_2S \rightleftharpoons COS + H_2O \tag{2-32}$$

$$H_2S + {}^3\!/_2O_2 \rightleftharpoons SO_2 + H_2O \tag{2-37}$$

Small quantities of CO_2 and CH_4 are present in any H_2S stream.

The quantities of CS_2 and COS generated are very small in comparison to the SO_2 quantity; CS_2 and COS become important, however, since quantitative recovery of sulfur is needed. The quantity of COS formed is usually close to its thermodynamic equilibrium value for furnace flame conditions. But CS_2 concentrations are often hundreds or thousands of times higher than the author's calculated equilibrium values (2-107). The amount of CS_2 formed is a strong function of the hydrocarbon concentration in the acid gas feed.

The relative quantities of SO_2 and elemental sulfur formed are determined by the combustion temperature of the furnace. The reaction that forms SO_2 becomes faster at higher temperatures than the reaction that forms sulfur. Therefore, the furnace is generally maintained at a temperature which will best compromise cooling requirements with sulfur conversion.

After the gas stream leaves the furnace, the elemental sulfur is removed from the stream and the remaining gas - a 2:1 mixture of H_2S and SO_2 - is sent to a catalytic converter at 218°C (2-108). The H_2S and SO_2 react to yield H_2O and S_2 according to Equation 2-20. This reaction has been found to give optimum conversion of H_2S to sulfur at low temperatures. However, the gas stream must be maintained above the sulfur dewpoint at converter conditions, or the liquid sulfur condensate will poison the catalyst.

Three catalytic converters are often used in the Claus gas phase process. The most common catalysts are alumina and bauxite, but sometimes special catalysts are used in one or more of these converters for the purpose of hydrolyzing COS and CS_2. Another common practice is operating the first catalytic reactor at a relatively high temperature, around 400°C, to hydrolyze COS according to Equation 2-35. High temperature operation in this first converter must be compensated for by operating the suceeding reactors closer to the dewpoint if overall sulfur recovery is to remain high. Each converter is followed by a condenser to remove sulfur, driving the Claus equilibrium closer to completion.

Tail gases from a Claus plant usually contain H_2S, SO_2, elemental sulfur, COS, and CS_2. The total concentration of sulfur is about 15,000 ppm, taken as SO_2 in an incinerated tail gas (2-109).

Split Flow Process

The split flow process, also called the modified Claus process, is the most widespread process for converting concentrated H_2S streams to elemental sulfur. In this form of the Claus process, one-third of the acid gas feed stream is diverted and then completely oxidized to SO_2. The streams are again combined and sent to a catalytic converter where they react according to Equation 2-20. In this process, as in the straight-through process, the 2:1 stoichiometry must be maintained by careful monitoring of the air supply.

The split flow process has greatest utility when the H_2S concentration in the acid gas feed is relatively low, 20 to 25 volume percent. In these cases the H_2S concentration may not be able to support combustion if the entire gas stream is allowed to dilute the combustion products. If the acid gas stream contains relatively high concentrations of hydrocarbons, on the order of two to five percent, the split flow process allows two-thirds of the gas stream to avoid the furnace, producing less COS and CS_2 (2-110).

The split flow process is subject to the same side reactions and catalytic conversions as the straight-through process. Typical conversions for the catalytic units are (2-108, 2-111):

1 converter: about 80% recovery,
2 converters: 92-95% recovery,
3 converters: 95-96% recovery,
4 converters: 96-97% recovery.

Direct Oxidation

In this process the acid feed gas is burned directly over a bauxite catalyst. High temperatures, up to 1000°F, and high space velocities are used. In this way the conversion becomes controlled by kinetic factors; therefore, the limits of the Claus equilibrium do not apply to this combustion. Stoichiometry is again important; the 2:1 H_2S and SO_2 ratio must be maintained.

This process has its greatest utility with gas streams having H_2S concentrations of 15% or less; higher concentrations are more economically handled by the split flow process (2-112). The direct oxidation step is generally followed by conventional Claus catalytic converters, which convert the residual H_2S and SO_2 to elemental sulfur.

Sulfreen Process

The Sulfreen process is essentially the Claus process made more efficient by operating at lower temperatures. The H_2S and SO_2 are reacted over an alumina or activated carbon catalyst at 127-150°C - below the dewpoint of sulfur in the reactor (2-113). These catalysts are very effective adsorbents for sulfur. When the catalyst becomes saturated with the liquid sulfur, hot gas is used to desorb the sulfur and regenerate the catalyst.

While it is likely that little COS or CS_2 would be generated at the Sulfreen reaction temperatures, these by-products are not hydrolyzed to H_2S over the Sulfreen catalyst at these temperatures. Therefore, the loss of sulfur in the form of COS and CS_2 reduces overall recovery.

A variation of the Sulfreen process uses two stages. The first stage uses the tail gas H_2S and SO_2, adjusting the stoichiometric balance so that all of the SO_2 is consumed. In the second stage the residual H_2S is oxidized directly to sulfur.

2.3.2 Claus Reactions in Liquid Media

H_2S removal processes based on the Claus reaction have been developed for liquid phase applications. Both organic and inorganic media have been found practicable.

Two liquid phase processes have reached industrial scale usage: the Bureau of Mines citrate process and the IFP process. In the former an aqueous citric acid solution is used to absorb SO_2 and H_2S from the acid gas streams. The basic Claus reaction takes place in this medium although the actual chemistry involved is more complex. The IFP process is based on a catalyzed Claus reaction in polyethylene glycol, a relatively high molecular weight solvent. An activated complex of H_2S and SO_2 is formed with the metal catalyst.

Two experimental processes are currently in the development stages: the Wiewiorowski liquid sulfur and the ethylene glycol mono ether processes. Ethylenediamine and other nitrogen compounds catalyze the Claus reaction in the liquid sulfur medium at 120 to 160°C. In the ethylene glycol mono ether process, the ether acts as the catalyst while the amine provides nucleation or flocculation sites to minimize colloid formation.

All of these are generally applicable to streams of low H_2S concentrations, e.g., Claus tail gas streams; although the Citrate process is a potential substitute for the gas phase Claus process.

2.3.3 Other H_2S Removal Processes

A number of other processes for H_2S removal which are not based on the Claus reaction have been developed. Those that employ liquid inorganic reaction medium involve a coupled oxidation-reduction chemistry. Inorganic species are used to oxidize the H_2S, followed by air oxidation to regenerate the inorganic oxidant.

Absorption of H_2S by organic solutions and subsequent oxidation are the bases of processes best suited to remove the last traces of H_2S before incineration and venting to the atmosphere.

Several composite processes are also available on an industrial scale. These are so classified because they are composed of processes previously discussed.

In addition, hydrogen sulfide may be removed electrochemically or by reaction with liquid SO_2.

2.4 Other Gas Phase Reactions

This section briefly summarizes recently published information on the kinetics and chemistry of other gas phase reactions of potential interest in this program. This category includes possible side reactions in SO_2 reduction systems. Literature reviews and data compilations (2-114, 2-115, 2-116) should be consulted for information published prior to the period covered in this literature survey, Chemical Abstracts 1967 through June 1975.

The results of the literature search summarized below are grouped according to species involved. The order of discussion is:

1) reactions involving sulfur dioxide and gaseous species not dealt with in previous sections (SO_2 oxidation is not within the scope of this program),

2) reactions of sulfur vapor,

3) reactions of carbonyl sulfide,

4) reactions of carbon disulfide, and

5) reactions involving hydrogen sulfide not dealt with in previous sections.

Reactions Involving SO_2

Gayen et al. calculated the free energy changes and equilibrium constants for reactions in the CO_2-SO_2 system at one atmosphere, 600-1000°C, and CO_2/SO_2 mole ratios of 1.00-0.25 (2-117). The two significant reactions considered are presented below.

$$2SO_2 + CO_2 = CS_2 + 3O_2 \qquad (2\text{-}38)$$

$$CS_2 + CO_2 = 2COS \qquad (2\text{-}39)$$

Their calculations indicate that CS_2 formation in this system is very small.

The interaction of SO_2 and COS has been the subject of several recent studies. Pulse and semi-pulse methods were used to study catalytic effects in one study (2-118). George found no significant effect due to catalyst basicity on the reaction below:

$$2COS + SO_2 = 2CO_2 + (\frac{3}{x})S_x \qquad (2\text{-}40)$$

A mechanism was postulated for the reaction (2-119). Haas and Khalafalla reported 90% conversion of reactants in the presence of pure χ-Al_2O_3 at 400°C. Inclusion of transition metals in the catalyst decreased the interaction between COS and SO_2 (2-120).

Reactions of Sulfur Vapor

Information concerning the reactions of sulfur vapor with atomic and molecular oxygen, C, CO, CO_2 and CH_4 appeared in the recent literature.

In the combustion of S vapors in jet conditions at 360-460°C, the presence of H_2 or CH_4 was found to produce an inhibiting effect (2-121). The reaction rate of ground state S atoms with molecular oxygen to produce SO and O has been investigated by flash photolysis-resonance fluorescence (2-122) and spectroscopy in the vacuum-uv region at 295°K (2-123). Correlation of the rate data using an Arrhenius type equation over the range 252-423°K yielded, in $cm^3\ mole^{-1} sec^{-1}$, (2-122):

$$k = (2.24 \pm 0.27) \times 10^{-12} \exp[(-0.00 \pm 0.10\ \text{kcal/mole})/RT] \quad (2\text{-}41)$$

The absolute reaction rate measured at 295°K was $1.0 \times 10^{12} cm^3\ mole^{-1} sec^{-1}$ (2-123); this value was reported to agree well with earlier results.

Investigations of the interaction of sulfur vapor and various forms of carbon have dealt with kinetics (2-124 - 2-126), mechanisms (2-125, 2-127), and parameters such as pressure, temperature, and bed height (2-124, 2-126, 2-128). The range of temperatures included in these studies was 500 to 1000°C. The chief product was CS_2, with some evidence of CS at high temperatures (>1000°C) which subsequently underwent rapid polymerization.

Bechtold studied the kinetics of the reaction between CO and S on platinum wires in a flow system at 300-450°C (2-129). The only reaction product detected was COS. Rate was dependent on temperature, degree of coverage of the Pt surface with S, and, depending on the first two parameters, CO and/or S pressure.

The mechanism of sulfur formation in the flash photolysis of carbonyl sulfide diluted in CO_2 was investigated (2-130). The formation and removal of S_2 takes place according to the following scheme:

$$2S_2 + CO_2 = S_4 + CO_2 \quad (2\text{-}42)$$

$$S + S_4 = S_2 + S_3 \quad (2\text{-}43)$$

$$S + S_3 = 2S_2 \quad (2\text{-}44)$$

The rate constant for the first of these reactions was determined to be $\sim 1 \times 10^{-29} cm^6 mole^{-2} sec^{-1}$.

The kinetics of the homogeneous reaction between sulfur and methane was reported to be first order with respect to both reactants in the range 600-700° (2-131). The reaction rate constant k expressed as (mole CS_2) $cm^{-3} hr^{-1} atm^{-2}$ is

$$k = 2.95 \times 10^8 \exp(-44.0 \times 10^3 RT). \quad (2\text{-}45)$$

Leszczynski and Kubica calculated thermodynamic parameters for the reaction

$$CH_4 + 4S = CS_2 + 2H_2S \quad (2\text{-}46)$$

in the range 25-1227°C (2-132). They determined the following reaction rate constant:

$$k = 7.29 \times 10^9 \, (P/RT)^2 \exp(-27{,}390/RT) \quad (2\text{-}47)$$

The units were not available in the abstract. The catalyzed synthesis of CS_2 from S vapor and methane was the subject of another experimental investigation (2-133). An equation for calculating the rate was proposed.

Reactions Involving Carbonyl Sulfide

The gas phase chemistry of COS summarized below includes thermal decomposition and interactions with hydrogen, sulfur vapor, water vapor, and oxygen.

The high temperature (2000-3200°K) kinetics of COS pyrolysis in argon atmosphere was studied in shock tube experiments (2-134). The principal species monitored were COS, CO, S, S_2, CS, and SO. Mechanisms, rate constants for the proposed reaction schemes, and activation energies were reported. Haas and Khalafalla studied the catalyzed decomposition in an integral reactor (2-120). The apparent activation energy measured in an uncatalyzed system was 28.7 kcal $mole^{-1}$. This value was reduced to 5.6 kcal $mole^{-1}$ when catalyzed with Al_2O_3 or SiO_2. Below 635°C the main products were CO_2 and CS_2, while at higher temperatures CO and S were produced. In another study supplementary reactions of COS decomposition and catalytic effects were investigated using pulse and semi-pulse methods (2-118).

Donovan measured rate constants which represent the sum of reaction and collisional relaxation for COS and H_2 in vacuum uv photolysis; the constants were 1.0×10^{-11} and 4.0×10^{-15} $cm^3 mole^{-1} sec^{-1}$, respectively (2-135). The kinetics of the reactions of hydrogen atoms with COS were measured at 25°C in a flow system (2-136). The rate constant was $2.2 \times 10^{-14} cm^3$ $particle^{-1} sec^{-1}$. At all COS flow rates H_2S is a major product, CO production equals COS consumption, and 0.5 mole of COS are consumed per H atom.

Reaction rates of COS with ground-state atomic sulfur (^3P) between 233 and 445°K, S(^1D) atoms, and S(3^1D_2) atoms in the presence of SF_6 have been studied (2-137, 2-138, and 2-139, respectively). The reaction shown below was reported to take place, and lower limits for the rate constant were established (2-138).

$$S(^1D) + COS = S_2 + CO \qquad (2\text{-}48)$$

The reaction between COS and H_2O proceeds according to the reaction below.

$$COS + H_2O = CO_2 + H_2S \qquad (2\text{-}49)$$

Pulse and semi-pulse methods were employed to examine roles of supplementary reactions of the hydrolysis. Hydrated Al_2O_3 and SiO_2 catalysts were both found to be active (2-118). George reported that catalyst basicity increased the initial reaction rate (2-119).

Rate constants were measured for the reaction of ground state atomic oxygen with carbonyl sulfide.

$$O + COS = CO + SO \qquad (2\text{-}50)$$

The rate constant in the Arrhenius form between 290 and 465°K is given, in $cm^3mole^{-1}sec^{-1}$, as (2-140):

$$k = 1.2 \times 10^{14} \exp(-5800 \text{ cal mole}^{-1}/RT) \qquad (2\text{-}51)$$

Correlation of rate data between 263 and 502°K yielded (2-141):

$$k = (1.65 \pm 0.13) \times 10^{-11} \exp(-4305 \pm 55/RT) \text{ in } cm^3mole^{-1}sec^{-1} \quad (2\text{-}52)$$

An inhibiting effect of H_2 and CH_4 on combustion of COS vapor in jet conditions at 360-460°C and 4-6 torr was observed by Sarkisyan et al. (2-121).

Reactions of Carbon Disulfide

Hildebrand studied the gas phase equilibrium of the reaction

$$CS_2 + S = CS + S_2 \qquad (2\text{-}53)$$

by mass spectrometry (2-142). The dissociation energy $D_0^\circ(CS)$ and heat of formation $H^\circ_{f_{298}}(CS)$ were determined: 166.1 ± 2 kcal and 70.0 ± 2 kcal $mole^{-1}$, respectively.

The presence of H_2 or CH_4 produced an inhibiting effect on CS_2 vapor combustion in jet conditions at 360-460° and 4-6 torr (2-141). Methane produces a greater inhibiting effect. The relationship between the concentration of O atoms and the concentration of H_2 in a CS_2 flame was given.

Reactions of Hydrogen Sulfide

Kinetic information was found for the gas-phase reactions involving H_2S with hydrogen and oxygen.

Rommel reported the rate constants of the reaction with hydrogen atoms at 298°K to be $3.8 \times 10^{-13} cm^3 particle^{-1} sec^{-1}$ (2-136). At high flow rates of H_2S 0.5 moles of H_2S are consumed per H atom originally present. The rate expression in Arrhenius form over the range 190-464°K reported by Kurylo et al. (2-143) in $cm^3 mole^{-1} sec^{-1}$ was:

$$k = (1.29 \pm 0.15) \times 10^{-11} \exp[-(1709 \pm 60)/1.987T] \qquad (2\text{-}54)$$

This was obtained under conditions which favored only the H atom - H_2S reaction. Mihelcic and Schindler conducted an ESR spectroscopic study of the reaction (2-144). In the -30 to

95°C range the activation energy was 1680 cal $mole^{-1}$. Rate constants for the following reactions were determined at 300°K:

Reaction	Rate Constant ($cm^3 mole^{-1} sec^{-1}$)	
$H + H_2S = H_2 + SH$	1.0×10^{-12}	(2-55)
$SH + SH$ [illegible] $H_2S + S$	1.1×10^{-11}	(2-56)
$S + SH = S_2 + H$	4.5×10^{-11}	(2-57)

The experimental frequency factor A was reported to be 1.7×10^{-11} $cm^3 mole^{-1} sec^{-1}$, which agreed well with the predicted value.

Assuming a stoichiometry of 3.5 atoms O per mole H_2S, the specific rate constant for the reaction $O + H_2S = OH + HS$ was $(1.74 \pm 0.40) \times 10^{11} \exp -(1500 \pm 100/RT)$ in $cm^3 mole^{-1} sec^{-1}$ (2-145). Takahashi studied the chemiluminescent reaction between H_2S and atomic O in a flow system at room temperature and 4-6 torr (2-146). The reaction scheme proceeded as follows:

$$H_2S + O = HS + OH \qquad (2\text{-}58)$$

$$HS + O = SO + H \qquad (2\text{-}59)$$

$$H + H_2S = H_2 + HS \qquad (2\text{-}60)$$

The rate constant of the first reaction was evaluated as 3.52×10^{-14} $cm^3 mole^{-1} sec^{-1}$.

3.0 COMMERCIAL PROCESSES FOR PRODUCTION OF ELEMENTAL SULFUR FROM MAGNESIUM SULFITE OR SULFUR DIOXIDE

In this section process schemes, equipment types, and operating conditions as reported in the literature are given for existing MgO regeneration and SO_2 reduction processes. Information on the following processes is presented in this section:

- MgO recovery from MgO flue gas desulfurization systems
- Allied Chemical SO_2 reduction system
- Asarco-Phelps Dodge elemental sulfur process
- Elemental sulfur production from pyrite
- Magnesium-base recovery process in the pulping industry

No existing process for direct conversion of magnesium sulfite to elemental sulfur was found.

3.1 The Current Operation of the Magnesium Oxide Recovery Process for the MgO Scrubbing Plants

A commercial calciner is presently being used at the Essex Chemical Company sulfuric acid plant in Rumford, Rhode Island, to regenerate MgO for a stack gas SO_2 removal process. Details of this process are shown in Figures A3-1 and A3-2. The calciner is a direct fired, refractory lined, counter-current rotary kiln (7'6" diameter by 120' long).

Temperatures at the middle of the calciner are kept at approximately 677°C (1250°F). The calciner operates at essentially atmospheric pressure. The calciner feed solids are primarily $MgSO_3$ with some $MgSO_4$ and unreacted MgO. A typical calciner feed composition is given in Table A3-1 (3-14).

TABLE A3-1

TYPICAL CALCINER FEED COMPOSITION

$MgSO_3$	63.9%
$MgSO_4$	12.7%
MgO	2.8%
Water and Inerts	21.0%

Impurities enter the system along with the make-up MgO and water streams. A typical composition of commercially produced make-up MgO is given in Table A3-2 (3-1).

TABLE A3-2

COMPOSITION OF CALCINED MAGNESITE

MgO	97-99%
CaO	0.55-1.0%
SiO_2	0.2 -0.4%
Fe_2O_3	0.05-0.25%
Al_2O_3	0.04-0.20%

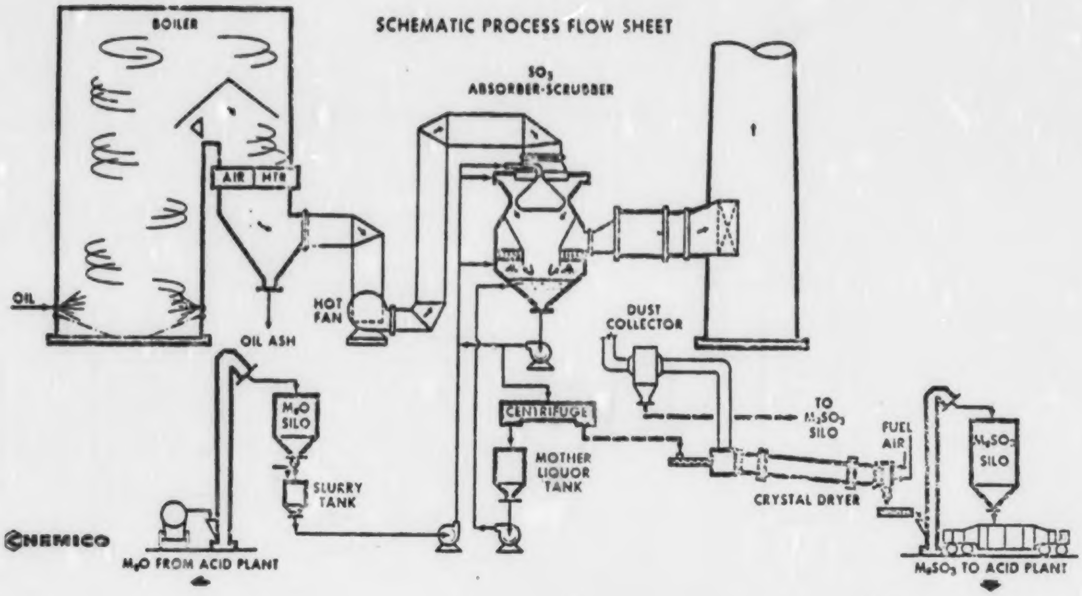

SCHEMATIC PROCESS FLOW SHEET
BOILER
AIR HTR
OIL
OIL ASH
HOT FAN
SO$_2$ ABSORBER-SCRUBBER
DUST COLLECTOR
TO MgSO$_3$ SILO
CENTRIFUGE
MOTHER LIQUOR TANK
MgO SILO
SLURRY TANK
FUEL AIR
CRYSTAL DRYER
MgSO$_3$ SILO
CHEMICO
MgO FROM ACID PLANT
MgSO$_3$ TO ACID PLANT

FIGURE A3-1 (3-4)

MgO ADDITIVE SCRUBBER SYSTEM FOR SO$_2$ RECOVERY, OIL FIRED BOILER

SCHEMATIC PROCESS FLOW SHEET

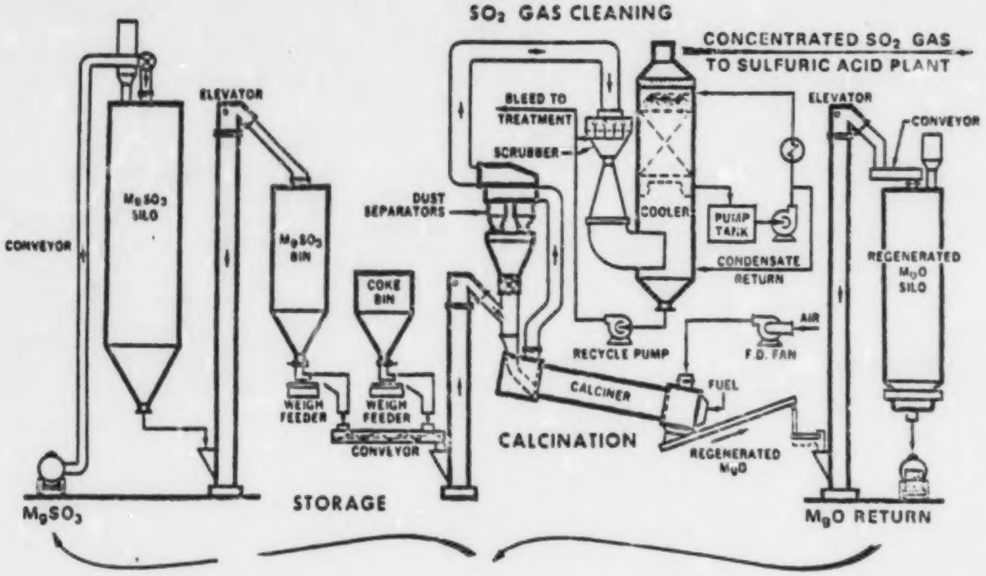

SO₂ GAS CLEANING
CONCENTRATED SO₂ GAS TO SULFURIC ACID PLANT
BLEED TO TREATMENT
SCRUBBER
DUST SEPARATORS
COOLER
PUMP TANK
CONDENSATE RETURN
RECYCLE PUMP
F.D. FAN
AIR
FUEL
CALCINER
CALCINATION
REGENERATED MgO
ELEVATOR
CONVEYOR
MgSO₃ SILO
MgSO₃ BIN
COKE BIN
WEIGH FEEDER
WEIGH FEEDER
CONVEYOR
CONVEYOR
ELEVATOR
CONVEYOR
REGENERATED MgO SILO
MgSO₃
STORAGE
MgO RETURN

FIGURE A3-2 (3-4)

REGENERATION SYSTEM MgO RECYCLE PROCESS,
FOR PRODUCTION OF 98% SULFURIC ACID

Calcination is performed by counter-current contact with combustion gases produced by burning No. 6 fuel oil with 5% excess air. Coke is added in the amount necessary to reduce the $MgSO_4$. The principal reactions in the calciner are (3-14):

$$MgSO_4 + C + \frac{1}{2}O_2 \rightarrow MgO + SO_2 + CO_2 \quad , \qquad (3\text{-}1)$$

$$MgSO_3 \rightarrow MgO + SO_2 \qquad (3\text{-}2)$$

The process yields 98% MgO with 2% impurities remaining in the solid product. The exit gas is a dilute stream of SO_2 whose approximate composition is given in Table A3-3 (3-2).

TABLE A3-3

TYPICAL CALCINER EXIT GAS COMPOSITION

N_2	73
CO_2	6
O_2	5
H_2O	7
SO_2	9

The residence time of the solid phase in the calciner is about one hour (3-2).

Operating problems which have been experienced with the rotary kiln include:

(1) Formation of periclase, an unreactive, "dead-burned" form of MgO at high operating temperatures. Pulverizing equipment was installed to activate the MgO and proved satisfactory.

(2) Excessive leakage at the seals of the rotary calciner which makes it difficult to maintain a reducing atmosphere. New seals which were recently designed and installed have apparently corrected this problem (3-3).

(3) Severe dusting in calciner which trips flame safety controls. An extra operator and flame scanner were necessary to solve this problem (3-3).

(4) Coke of low ash content (less than 10%) is needed to prevent contamination of the calcined solids and the product gas sent to the acid plant (3-3).

In the course of the calciner operation upsets have occasionally resulted in the formation of elemental sulfur. Attempts to reproduce these upset conditions in the laboratory have not as yet yielded any specific information on the formation of elemental sulfur(3-4).

3.2 Allied Chemical SO_2 Reduction System

Allied Chemical Corporation has developed and commercialized a process for direct, catalytic reduction of SO_2 to elemental sulfur using natural gas as a reductant. The first plant to use the process is located near Sudbury, Ontario, Canada. A process flow diagram of this facility is shown in Figure A3-3. The plant, which received a feedstock gas containing approximately 12% SO_2 from a sulfide-ore roasting facility, consists of three main sections: gas purification, SO_2 reduction, and sulfur recovery. The gas purification system, which is designed to remove excess water vapor and gaseous and solid impurities would be optional in certain applications (3-5).

The principle function of the catalytic reduction section is to increase the H_2S/SO_2 ratio in the gas stream to approximately the ideal ratio of 2:1 required for the Claus reaction, while achieving maximum formation of elemental sulfur. The primary reaction system may be summarized in the following equations:

$$CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + S_2 \qquad (3\text{-}3)$$

$$4CH_4 + 6SO_2 \rightarrow 4CO_2 + 4H_2O + 4H_2S + S_2 \qquad (3\text{-}4)$$

In the reduction section, the combined, preheated natural gas and SO_2 stream first passes through a four-way-flow reversing valve and a final preheat reactor. The heated stream then enters the primary reactor where over 40% of the total recovered sulfur is formed (3-6). The reactor uses a catalyst developed by Allied Chemical that is stable up to 1093°C (2000°F), achieves efficient methane utilization, and provides minimum formation of undesirable side products (3-5). Careful control of the reaction conditions is necessary to achieve chemical equilibrium in the single reactor.

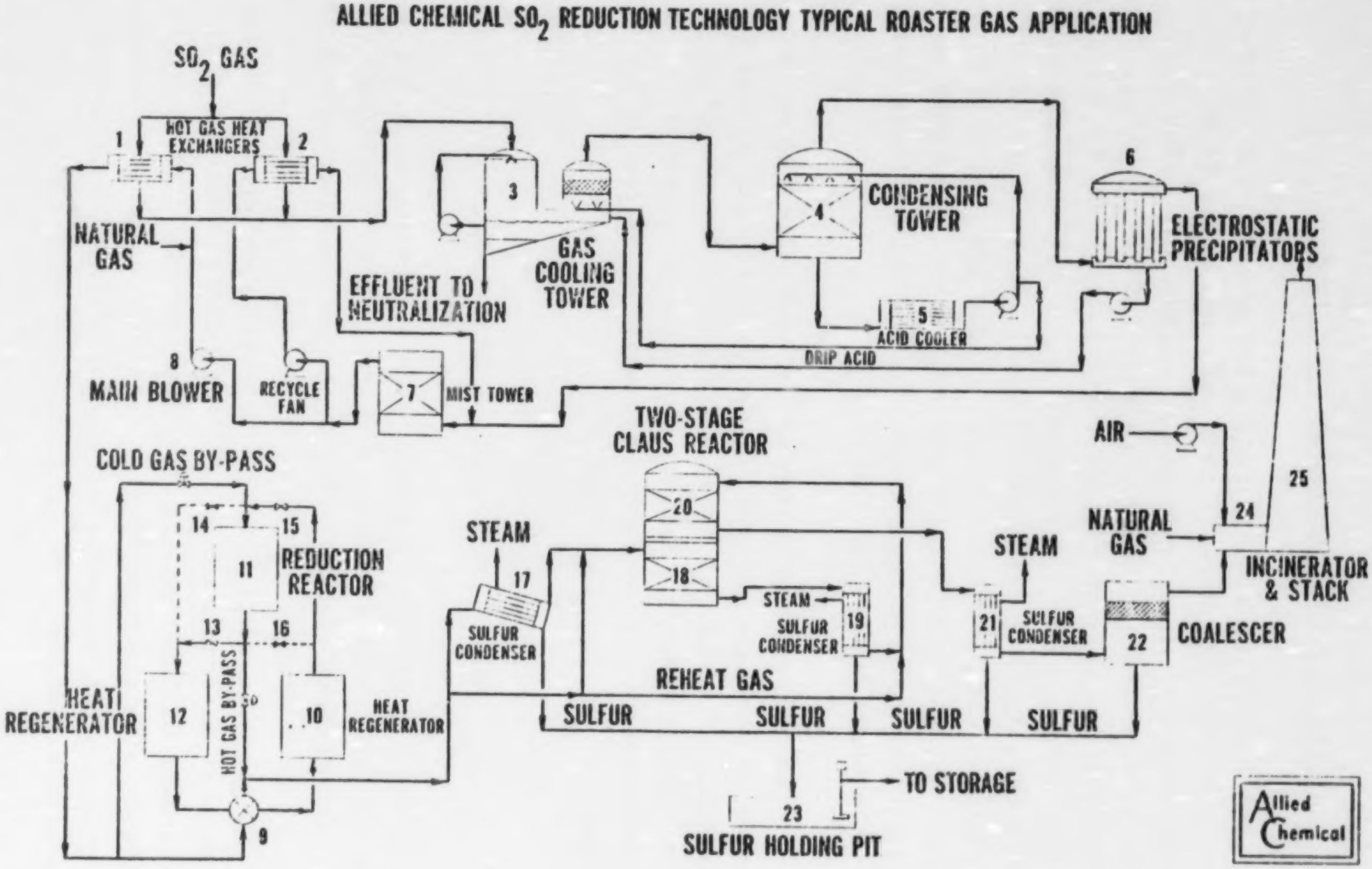

ALLIED CHEMICAL SO2 REDUCTION TECHNOLOGY TYPICAL ROASTER GAS APPLICATION
SO2 GAS
HOT GAS HEAT EXCHANGERS
1
2
NATURAL GAS
3
GAS COOLING TOWER
EFFLUENT TO NEUTRALIZATION
4
CONDENSING TOWER
5
ACID COOLER
DRIP ACID
6
ELECTROSTATIC PRECIPITATORS
8
MAIN BLOWER
RECYCLE FAN
7
MIST TOWER
TWO-STAGE CLAUS REACTOR
AIR
25
24
NATURAL GAS
INCINERATOR & STACK
COLD GAS BY-PASS
14
15
11
REDUCTION REACTOR
13
16
HOT GAS BY-PASS
HEAT REGENERATOR
12
10
HEAT REGENERATOR
9
STEAM
17
SULFUR CONDENSER
20
18
STEAM
SULFUR CONDENSER
19
STEAM
21
SULFUR CONDENSER
22
COALESCER
REHEAT GAS
SULFUR
SULFUR
SULFUR
SULFUR
23
SULFUR HOLDING PIT
TO STORAGE
Allied Chemical

FIGURE A3-3 (3-8)

ALLIED CHEMICAL SO_2 REDUCTION TECHNOLOGY, TYPICAL ROASTER GAS APPLICATION

The gas leaving the reduction reactor passes through a second heat regenerator, where it gives up its heat to the packing. Direction of flow through the two heat regenerators is periodically reversed, to interchange their functions of heating and cooling.

After condensing sulfur in a steam generator, the gas stream enters a two-stage Claus reactor system where H_2S and SO_2 react to produce elemental sulfur and water. At this point, product sulfur is again removed from the gas by condensation. Residual H_2S in the Claus plant effluent gas is oxidized to SO_2 in an incinerator before it is exhausted through stack to the atmosphere (3-6).

According to the developer, this process can be applied directly to SO_2 streams containing as low as 4% SO_2 where oxygen content is not over 5.0%. When higher oxygen concentrations are encountered, provisions must be made to dissipate the excess heat produced as a result of methane oxidation. The Canadian plant has demonstrated that this process is capable of removing better than 90% of the SO_2 from the entering gas stream. Operation at one-third of design capacity with constant operating efficiency has been established (3-7).

3.3 Asarco-Phelps Dodge Elemental Sulfur Pilot Plant

A 20 tpd elemental sulfur pilot plant has been tested by Asarco at their El Paso copper-lead smelter (3-9). The Asarco process utilizes a feed gas stream containing a minimum SO_2 concentration of 10-15% and a maximum O_2 concentration of 2-3%. A flow diagram for this process is shown in Figure A3-4. A reforming process developed by Phelps Dodge Corporation was used in the pilot facility to produce a reducing gas stream containing a 48-50% mixture of CO and H_2.

In the Asarco process, the reformed gas and SO_2 were stoichiometrically combined and introduced into a primary catalytic reactor at approximately 343°C (650°F). This reactor was a vertical shell-and-tube heat exchanger with the tubes filled with catalyst. Since the reduction of SO_2 is highly exothermic, and an organic heat transfer fluid was circulated through the shell side of the vessel to control reaction temperature. The heated coolant was used to generate steam and reheat the process gas stream entering the second catalytic reactor. The gas stream leaves the primary reactor essentially at equilibrium. Approximately 69% conversion of SO_2 to sulfur vapor was obtained when treating a 12% SO_2 stream.

Tail gases from the primary reactor were cooled in a condenser to recover liquid sulfur and then reheated to about 204°C (400°F) and passed through a Claus reactor. This step utilized a catalytic, fixed bed reactor with no internal cooling provided. In the second stage reactor, SO_2 and H_2S react to yield additional sulfur which is recovered in a second condenser.

Total sulfur recovery averaged 88-92% over 91 days of semi-continuous operation. One major problem involved in the

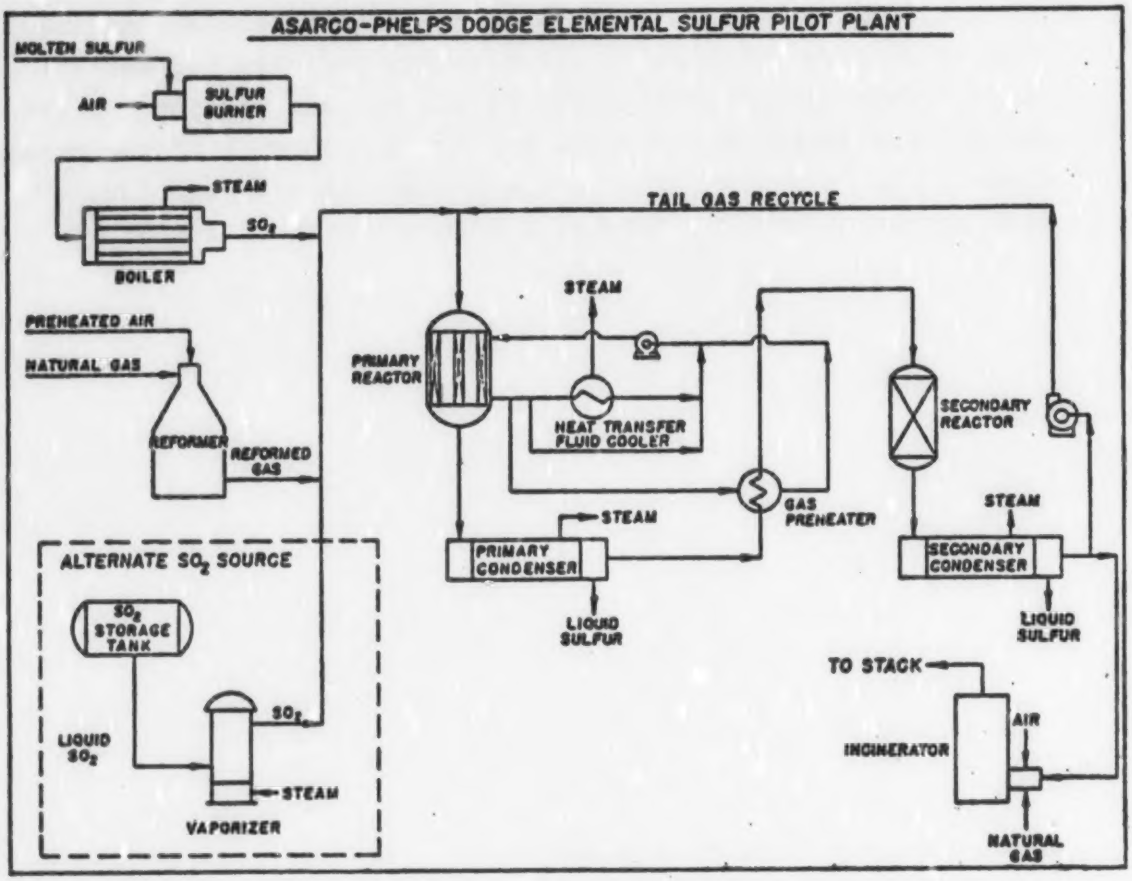

ASARCO-PHELPS DODGE ELEMENTAL SULFUR PILOT PLANT
MOLTEN SULFUR
AIR
SULFUR BURNER
STEAM
BOILER
SO_2
TAIL GAS RECYCLE
STEAM
PRIMARY REACTOR
PREHEATED AIR
NATURAL GAS
REFORMER
REFORMED GAS
HEAT TRANSFER FLUID COOLER
SECONDARY REACTOR
GAS PREHEATER
STEAM
PRIMARY CONDENSER
LIQUID SULFUR
STEAM
SECONDARY CONDENSER
LIQUID SULFUR
ALTERNATE SO_2 SOURCE
SO_2 STORAGE TANK
LIQUID SO_2
SO_2
STEAM
VAPORIZER
TO STACK
AIR
INCINERATOR
NATURAL GAS

FIGURE A3-4 (3-9)

ASARCO-PHELPS DODGE ELEMENTAL SULFUR PILOT PLANT reducing operation was decrepitation of catalyst pellets in the first few inches of the catalyst bed in the primary reactor. No loss of catalyst activity was detected, but there was an increased resistance to gas flow.

Thermal decomposition of the organic coolant in the primary reactor resulted in solid carbon deposits between the tubes. This caused overheating in the blocked portions of the reactor and subsequent warpage and burning through of the tube sheet. The installation of a new primary reactor and further test operation were planned as a future course of action.

3.4 Sulfur Production at a Pyrite Smelting Plant

Outokumpu Oy Company is operating a pyrite smelting plant in Finland that converts pyrite feed into elemental sulfur and iron oxide pellets (3-10). The plant produces 90,000 tons/yr of elemental sulfur and 250,000 tons/yr of iron oxide pellets. A process flow diagram for this system is shown in Figure A3-5. Pyrite concentrate (FeS_2)is fed to a flash-smelting furnace. The combustion of Bunker C fuel oil is carried out without any soot formation in a specially designed furnace having three high-efficiency burners. Incoming pyrites are suspended in the hot reducing gases and fed to the smelter where thermal decomposition takes place at about 1800°C (3270°F).

Reaction gases (CO_2, H_2O, N_2, SO_2, H_2S, CO, H_2), dust, and sulfur vapors are cooled in a radiation chamber (high pressure steam boiler) and a convection chamber. This cooling operation shifts the equilibrium of the gas components to maximize sulfur content.

In the radiation chamber the gases are cooled to 600°C (1110°F) where CO and H_2 react with SO_2 to yield S_2 and H_2S. During a second cooling step down to about 300°C (570°F), H_2S and SO_2 react to form elemental sulfur. Sulfur yield is optimized by passing the gases at 270-277°C (518-530°F) over an aluminum-based catalyst in a catalytic reactor downstream of the low pressure boiler. Separation of elemental sulfur from the combustion gases takes place in a cooling tower where molten sulfur circulates over the gas stream. A second washing step with seawater removes small amounts of sulfur remaining in the reaction gases.

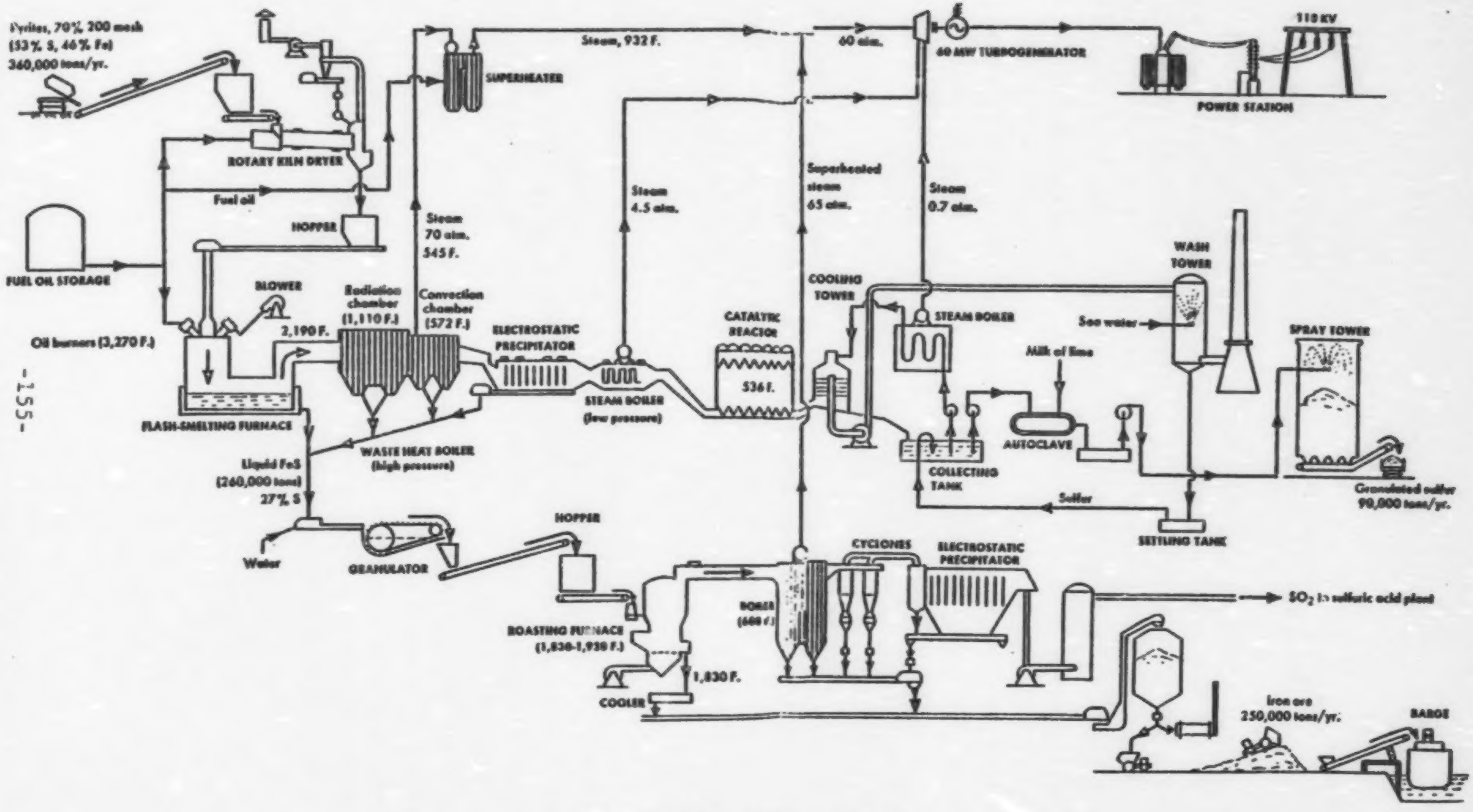

Pyrites, 70% 200 mesh
(53% S, 46% Fe)
360,000 tons/yr.
ROTARY KILN DRYER
Fuel oil
HOPPER
FUEL OIL STORAGE
BLOWER
Oil burners (3,270 F.)
2,190 F.
Radiation chamber (1,110 F.)
Convection chamber (572 F.)
Steam 70 atm. 545 F.
SUPERHEATER
Steam, 932 F.
FLASH-SMELTING FURNACE
WASTE HEAT BOILER (high pressure)
ELECTROSTATIC PRECIPITATOR
STEAM BOILER (low pressure)
Steam 4.5 atm.
CATALYTIC REACTOR
536 F.
Superheated steam 65 atm.
60 atm.
60 MW TURBOGENERATOR
110 KV
POWER STATION
Steam 0.7 atm.
COOLING TOWER
STEAM BOILER
WASH TOWER
Sea water
Milk of lime
AUTOCLAVE
COLLECTING TANK
SPRAY TOWER
Granulated sulfur 90,000 tons/yr.
Sulfur
SETTLING TANK
Liquid FeS (260,000 tons) 27% S
Water
GRANULATOR
HOPPER
ROASTING FURNACE (1,830-1,920 F.)
1,830 F.
COOLER
BOILER (680 F.)
CYCLONES
ELECTROSTATIC PRECIPITATOR
SO2 to sulfuric acid plant
Iron ore 250,000 tons/yr.
BARGE

FIGURE A3-5 (3-10)

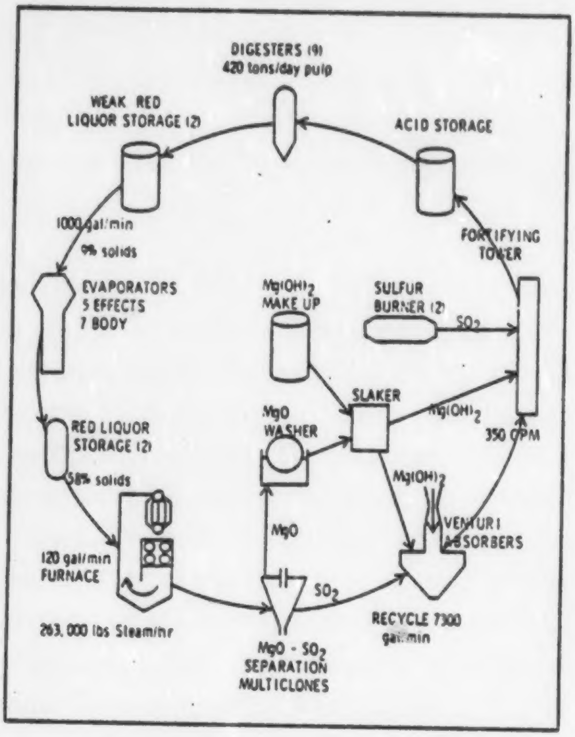
PROCESS FOR CONVERSION OF PYRITE TO ELEMENTAL SULFUR AND IRON OXIDE

3.5 The Magnesium-Base Recovery Process in the Pulping Industry

Magnesium-base pulping with chemical recovery is practiced in paper mills in North America and Europe. Most of these mills use the magnesium bisulfite process ("magnefite"). In this study, the process step that regenerates magnesium oxide is of interest. The details of this process are shown in Figure A3-6.

Magnesium base liquor from the pulping operation, containing 50-65% lignosulfonate and the rest sugars and acids, is concentrated to about 55% total dissolved solids (3-12). Magnesium oxide ash is then recovered by burning the residue in a furnace or a fluidized bed combustion chamber. The design of the combustion chamber used to burn this material is important in order to maintain the required properties of the MgO ash. Combustion must be complete to produce a carbon free ash. At the same time however, overheating of the MgO must be avoided since this produces an unreactive, dead burned, form of MgO called periclase. This crystalline form of the oxide cannot be used in liquor regeneration.

The Babcock and Wilcox recovery units use a high temperature furnace where fuel evaporation and combustion take place. Hot liquor is sprayed into the furnace by means of steam atomizing nozzles. Combustion temperatures are controlled so that the flue gases leave the combustion chamber at a temperature above 1300°C (2372°F) to assure an essentially carbon-free ash. The magnesium oxide ash is separated from the flue gas with cyclonic collectors which have an 80-95% efficiency. The remainder of the ash is collected in the cooking liquor preparation plant, where magnesium hydroxide and sulfur dioxide in the flue gas are combined in gas-liquid contactors to regenerate the


DIGESTERS (9)
420 tons/day pulp
WEAK RED
LIQUOR STORAGE (2)
ACID STORAGE
1000 gal/min
9% solids
FORTIFYING
TOWER
EVAPORATORS
5 EFFECTS
7 BODY
Mg(OH)2
MAKE UP
SULFUR
BURNER (2)
SO2
SLAKER
Mg(OH)2
MgO
WASHER
350 GPM
RED LIQUOR
STORAGE (2)
58% solids
Mg(OH)2
VENTURI
ABSORBERS
MgO
120 gal/min
FURNACE
SO2
263,000 lbs Steam/hr
RECYCLE 7300
gal/min
MgO - SO2
SEPARATION
MULTICLONES

Magnefite chemical recovery cycle.

FIGURE A3-6 (3-11)

cooking liquor. In some installations, when the MgO ash is finer, electrostatic precipitators or a wet separator is used to recover the MgO (3-13).

An alternative system for decomposing waste cooking liquor to MgO and SO_2 is used at the Wausau Paper Mills Company in Brokaw, Wisconsin, where a fluidized bed combustion process has been installed. Liquid concentrated to 40% solids flows into a fluidized bed furnace operating at about 930°C (1706°F). This furnace contains a bed of granular magnesium oxide pellets fluidized by the combustion air entering at the bottom. The waste liquor decomposes to produce a flue gas containing SO_2. MgO ash remains in the reactor and becomes part of the bed. MgO pellets are continuously discharged from the bed to maintain a constant amount of bed material in the furnace. A cyclone is used to remove entrained ash from the flue gas (3-13).

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APPENDIX B

TECHNICAL NOTE 200-045-31-02

"THERMODYNAMIC SCREENING TO DETERMINE THE FEASIBILITY OF PRODUCING ELEMENTAL SULFUR FROM MAGNESIUM SULFITE"

TECHNICAL NOTE 200-045-31-02

THERMODYNAMIC SCREENING TO DETERMINE THE FEASIBILITY OF PRODUCING ELEMENTAL SULFUR FROM MAGNESIUM SULFITE

4 September 1975

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1.0 INTRODUCTION

The EPA is interested in the feasibility of producing elemental sulfur in the regeneration section of the magnesium oxide scrubbing process. This technical note examines the influence of various reducing gases on the decomposition of $MgSO_3$ to MgO and sulfur. The study will be restricted to looking at the thermodynamics of the system. The kinetics will be brought into the study later. Equilibrium calculations were made to determine the influence of temperature and stoichiometry on the gaseous and solid product distributions.

The first section of the note discusses the selection of the conditions and chemical species to be included in the equilibrium calculations. The second section contains the results and conclusions from the calculations.

The results of this technical note will be used as the basis for selecting process configuration(s) and general operating conditions.

2.0 DISCUSSION

A thermodynamic screening was made by calculating possible equilibrium concentrations of products from the calciner. The influences of temperature and stoichiometry using different reducing agents on gaseous and solid product distributions were determined. An overall heat balance for the calciner was also calculated.

A computer program was used on all equilibrium and heat calculations. The program determined chemical equilibrium by minimizing the free energy of the system. The input to the system in the program was one mole of $MgSO_3$ with the amount of the reducing gas determined by the desired stoichiometry. The temperature of the system was specified and the equilibrium composition was determined at 1.0 atm.

2.1 Selection of Equilibrium Conditions

The decomposition temperature of $MgSO_3$ is defined as the temperature at which the equilibrium partial pressure of SO_2 over solid $MgSO_3$ is 1 atm. Although this occurs at 360°C in an inert gas atmosphere, the reaction is fairly slow at this temperature. $MgSO_3$ decomposes rapidly above 500°C. Therefore, to insure that the lower temperature limit would be within the investigation range, a lower limit of 350°C was chosen.

From the literature search we see that the noncatalytic gas phase reactions which produce elemental sulfur using CO or H_2 as reducing agents do not proceed rapidly below 900°C (no significant conversion within several minutes). Catalysts lower the gas phase reaction temperature to the order of 400°C. In order to include noncatalytic temperatures of interest an upper limit of 1000°C was chosen. The discrete temperatures used in the equilibrium screening study are shown in Table B2-1.

Reducing gases of CO, H_2, CO + H_2, and CH_4 were selected on the basis of their relatively widespread availability and their previously known capability to reduce SO_2 to elemental sulfur. Coal and coke were not chosen because their reactive intermediates are probably CO and H_2. The kinetic limiting step may well be the coke or coal gasification step and is beyond the scope of this study.

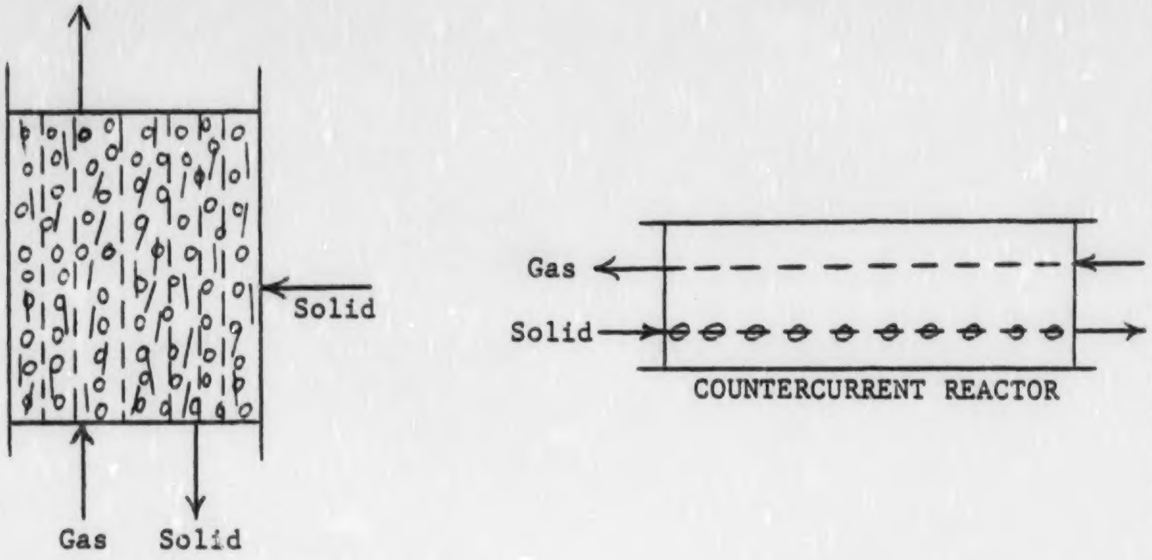
The stoichiometries of the reducing agents were varied to find the optimum stoichiometry for elemental sulfur production and to simulate possible different conditions in a reactor. Three major types of reactors were considered: fluidized bed, co-current, and countercurrent reactors. Figure B2-1 shows the directions of flow for the gas and solid phase in each reactor. An important point is that for co-current and fluidized bed reactors, the gas and solids leaving the reactor are in intimate contact. For countercurrent reactors they are not in contact.

Figure B2-2 shows the relative amounts of unreacted species present ($MgSO_3$ and the reducing gas) over the length of the reactor for the fluidized bed reactor. The solid composition is the same in all parts of the reactor because of its mixing characteristics. The gas composition becomes lower in unreacted reductant as it passes through the reactor from inlet to outlet.

TABLE B2-1

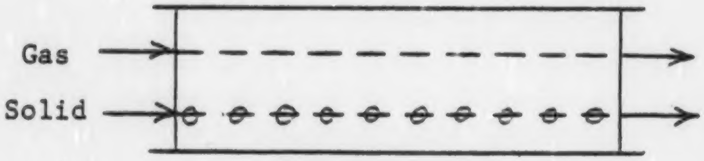
EQUILIBRIUM CASES

Temperature (^{o}C)	Stoichiometry	Reducing Gases
350	.95	100% CH_4
500	1.0	100% CO
700	1.05	100% H_2
1000	1.5	50% CO, 50% H_2
	20.0	


Solid
Gas
Solid
Gas
Solid

FLUIDIZED-BED REACTOR

COUNTERCURRENT REACTOR



COCURRENT REACTOR

FIGURE B2-1 - DIRECTIONS OF FLOW IN THREE TYPES OF REACTORS

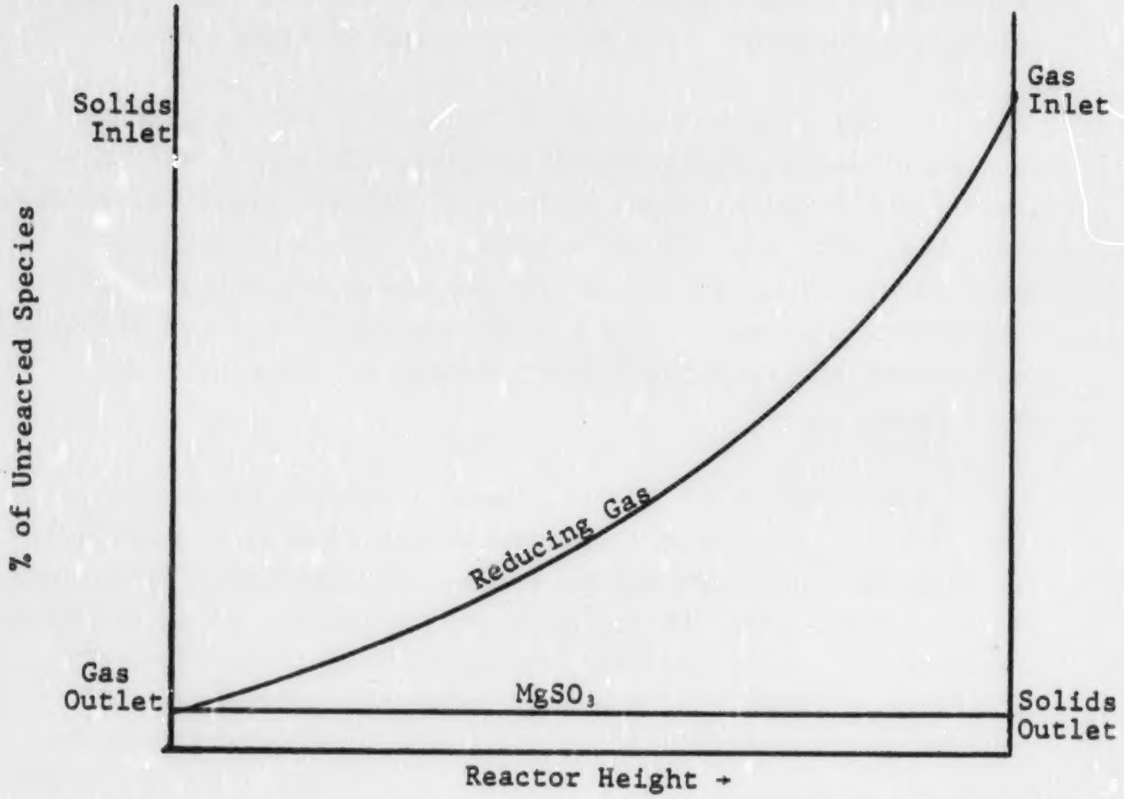


FIGURE B2-2 - REACTION DRIVING FORCE IN A FLUIDIZED BED REACTOR

In the countercurrent reactor depicted in Figure B2-3, the unreacted solids decrease steadily from inlet to outlet. The reacted solids at the outlet will "see" fresh reducing gas. The "spent" reducing gas leaving "sees" fresh solids. A cocurrent reactor is depicted in Figure B2-4.

The stoichiometries in Table B2-1 were chosen to represent several different conditions. Obviously stoichiometries with the minimum required to produce elemental sulfur, i.e., near 1.0, are of most interest. Values of 0.95, 1.0, and 1.05 are directed toward the gas phase and the product composition attainable. The stoichiometry of 1.5 was chosen to see what effect a significant excess of reducing agent would have.

The value of 20 was chosen primarily to investigate the solid effluent from a countercurrent reactor. Consider, for instance, the case of the overall stoichiometry being one and at a point near the solid exit. Choose the point at which the unreacted solid is five percent. The gas therefore contains twenty times the amount of reducing agent necessary. The chemical potentials of solids are not dependent upon the amount of various species present. In the gas phase the chemical potentials are dependent upon the amount present. For this reason the twenty to one stoichiometry was used to predict sulfiding, coking, and other tendencies at the solid exit of a countercurrent reactor.

A heat balance around the overall process was made by inputing the gas and solid streams at specified temperatures. A temperature of 25°C was chosen for the magnesium sulfite, which corresponds to the case in which $MgSO_3$ is dehydrated at a site separate from the calcining operation. If the $MgSO_3$ is dehydrated on site it would be at a higher temperature because it would pass from a dryer to the calciner.

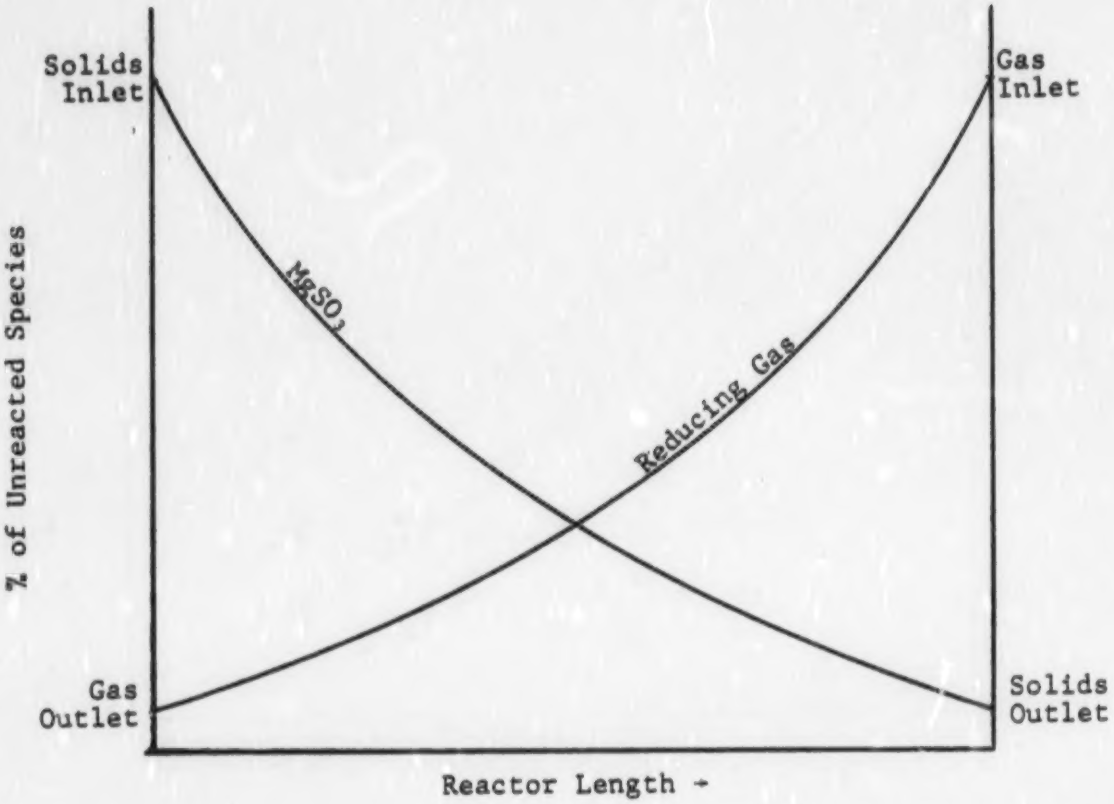


FIGURE B2-3 - REACTION DRIVING FORCE IN A COUNTERCURRENT REACTOR

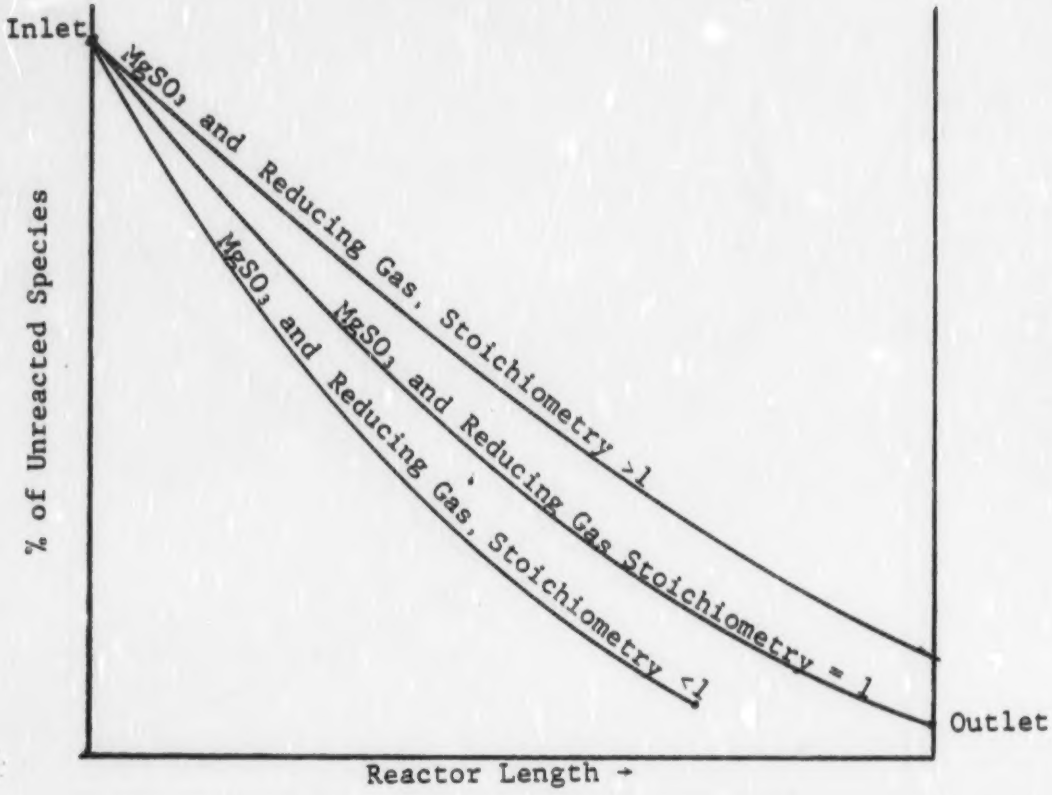


FIGURE B2-4 - REACTION DRIVING FORCE IN A COCURRENT REACTOR

Three of the reducing gases, H_2, CO, and the H_2/CO mixture, were specified to be at 1000°C. This temperature was chosen as a rough estimate of the reducing gases produced from a fuel combustion process. Methane was chosen to be 25°C since it would be obtained from a pipeline. The gas and solids leaving the reactor were assumed to be at the same temperature.

An enthalpy balance was made for the various reactions. The simplified scheme shown in Figure B2-8 was used. A major purpose of the calculations was to determine the adiabatic operating temperature of the reaction, i.e., the condition at which $Q = 0$. For cases where $Q < 0$ heat must be removed. For cases where $Q > 0$ heat must be added. To extrapolate the cases to different inlet temperature conditions, e.g., reducing gas at 500°C, the enthalpy difference in Kcal per Kg of total reactants must be subtracted from the calculated Q's to give values for the new conditions. For the example given the number to be subtracted is negative so the net result would be to make the reactions more endothermic (less exothermic).

The temperature profile in a fluidized bed reactor is shown in Figure B2-5. Fluidized bed reactors are characterized by isothermal operation because of high gas-solid heat transfer rates and good mixing. The profile shows that the gas and solid are at the same temperature everywhere within the reactor. The temperature profile for a countercurrent reactor is shown in Figure B2-6. The profile for this special case has the gas and solid leaving the reactor at the same temperature. Figure B2-7 shows a cocurrent reactor.

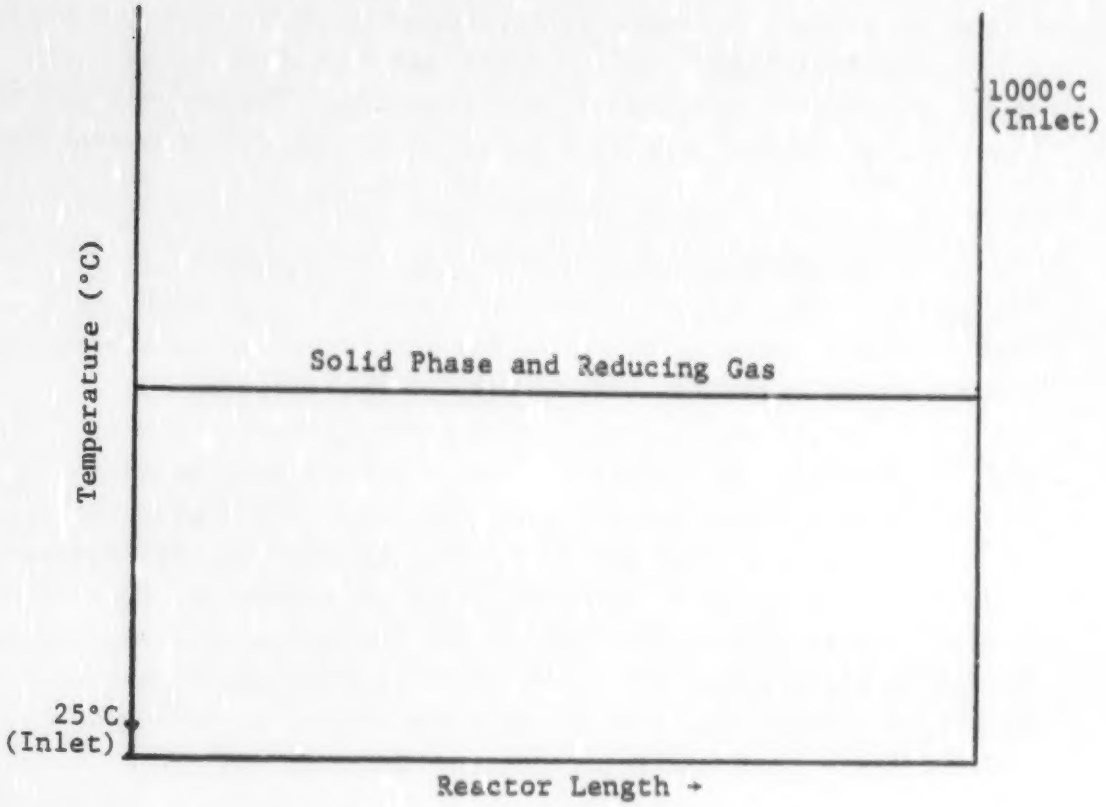


FIGURE B2-5 - TEMPERATURE PROFILE IN A FLUIDIZED BED REACTOR

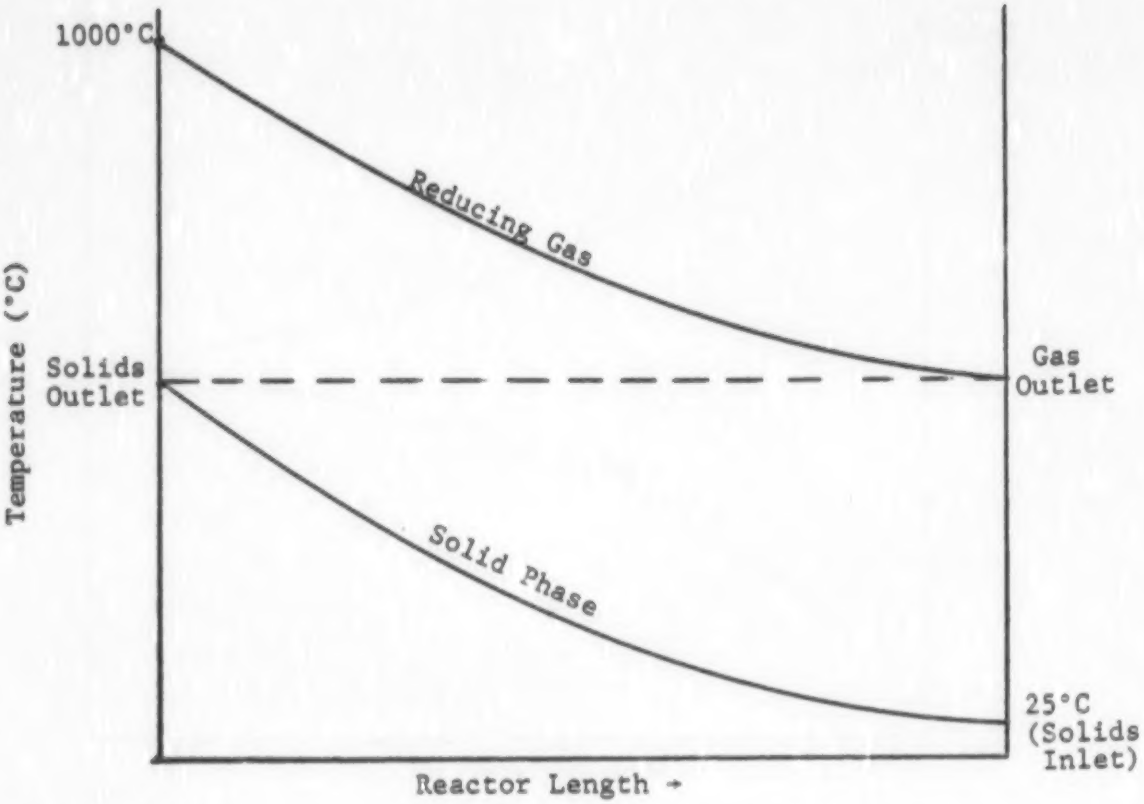


FIGURE B2-6 - TEMPERATURE PROFILE IN A COUNTERCURRENT REACTOR

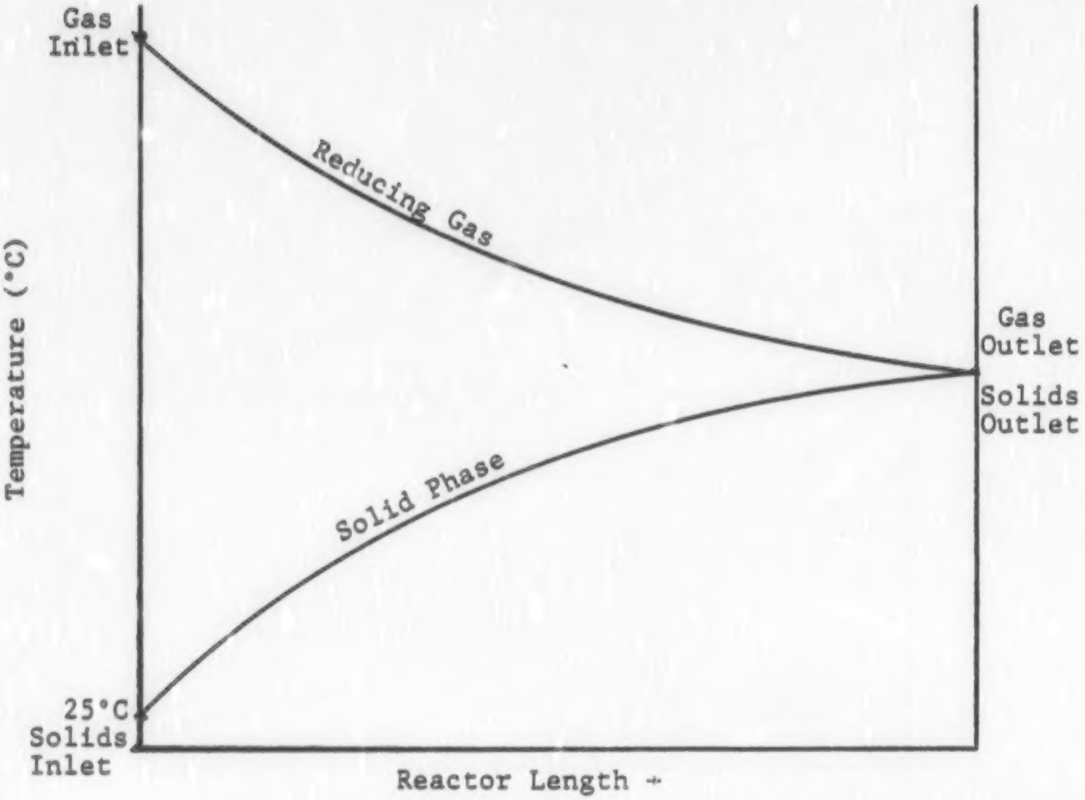


FIGURE B2-7 - TEMPERATURE PROFILE IN A COCURRENT REACTOR

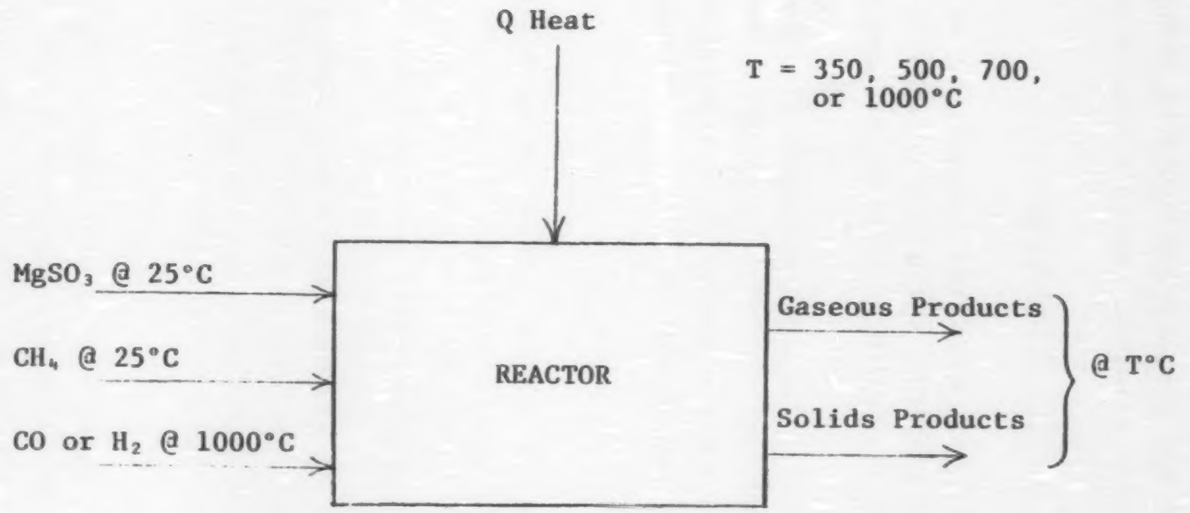

Q Heat
T = 350, 500, 700, or 1000°C
$MgSO_3$ @ 25°C
CH_4 @ 25°C
CO or H_2 @ 1000°C
REACTOR
Gaseous Products
Solids Products
@ T°C

FIGURE B2-8 - HEAT BALANCE SCHEMATIC

The results may also be used to some extent for investigating different exit conditions. The gas temperature may not be changed because it would alter the equilibrium mixture. The solid MgO temperature could be changed in a fashion similar to the reactant sensible heat changes.

2.2 Chemical Species Considered

As the stoichiometry and temperature are changed, the distribution of elements among the various species changes. Also, the solids in equilibrium with the gas can change.

The gas and solid species which were considered as being potentially present in this system are listed in Table B2-2. These species were selected on the basis of their probability of existing in the reactor as determined by the literature survey.

All of the gas species, with the exception of H, MgS, and S, were commonly seen experimentally and were included in thermodynamic calculations by investigators of SO_2 reduction systems. The above three species were included to check their possible presence at different conditions. The gas phase elemental sulfur species were assumed to be S_2 and S_8. While one investigator presented evidence that S_3, S_4, S_5, and S_7 also could exit in this system (ME-121), the thermodynamic data for these were not in the Radian data base.

The solid phase species MgO, $MgSO_3$, $MgSO_4$, and S (liquid) have been found in the magnesium oxide calciner used in Rumford, Rhode Island (KO-134). The MgS and MgS_2O_3 species were a subject of study in the Mg-SO_2-O_3

TABLE B2-2

CHEMICAL SPECIES CONSIDERED IN THERMODYNAMIC SCREENING

Gas		
H	CO	S
H_2	CO_2	S_2
H_2O	COS	S_8
H_2S	CS_2	SO_2
O_2	CH_4	SO_3
	MgS	

Condensed Phase	
MgO	$MgSO_3$
MgS	$MgSO_4$
S (liquid)	MgS_2O_3
C (graphite)	$MgCO_3$

system (SC-144). The two carbon containing species, $MgCO_3$ and C (graphite), were chosen to check their existence at high concentrations of reducing agents containing carbon.

For the majority of the species considered the thermodynamic quantities used in this study were obtained from the well-known JANAF Thermochemical Tables (ST-067). Data were estimated only for MgS_2O_3.

3.0 RESULTS AND CONCLUSIONS

This section presents a discussion of the results of the thermodynamic screening. Calculations for the four reducing gases at five stoichiometries and four temperatures were made (a total of 80 cases) as shown in Tables B3-1 through B3-8.

The $MgSO_3$ was completely decomposed in all of the cases. The main decomposition product was MgO. In the low-temperature, low-stoichiometry cases some $MgSO_4$ formation was predicted. This indicates that a temperature above 350°C but less than 500°C would be desirable from a solid product point of view. In none of the cases were MgS_2O_3 or MgS stable. There appears to be no danger of sulfide formation under reducing conditions.

When CO is used as a reducing gas a large percentage of the solid product appears as $MgCO_3$ at 350°C. The $MgCO_3$ compound is not a process problem since it would decompose during the scrubbing process to MgO and CO_2. It could be a shipping problem because $MgCO_3$ weighs twice as much as MgO.

The two reducing agents containing carbon, CH_4, and CO, have a large carbon formation tendency at high stoichiometries. Coke formation might be expected at the gas inlet to a fluid-bed or countercurrent calciner due to methane cracking or CO decomposition. If the process is catalytic the coking condition could be a problem.

TABLE B3-1

$MgSO_3$ DECOMPOSITION WITH CH_4 REDUCTANT

Case	Stoic.	Temp. (°C)	(Fraction of total sulfur in each species)						
			S_2	S_8	SO_2	H_2S	COS	CS_2	$MgSO_4$
1	.95	350	.004	.489	.002	.354	0	0	.151
2	.95	500	.200	.354	.182	.263	.001	0	0
3	.95	700	.554	0	.184	.259	.004	0	0
4	.95	1,000	.657	0	.167	.171	.006	0	0
5	1.0	350	.005	.487	.014	.378	0	0	.117
6	1.0	500	.203	.348	.150	.297	.001	0	0
7	1.0	700	.554	0	.150	.291	.004	0	0
8	1.0	1,000	.663	0	.134	.196	.007	0	0
9	1.05	350	.005	.497	.014	.395	0	0	.089
10	1.05	500	.205	.336	.120	.337	.002	0	0
11	1.05	700	.548	0	.120	.328	.005	0	0
12	1.05	1,000	.662	0	.105	.225	.008	0	0
13	1.5	350	.001	.001	0	.990	.007	0	0
14	1.5	500	.016	0	0	.959	.025	0	0
15	1.5	700	.125	0	0	.820	.054	.001	0
16	1.5	1,000	.347	0	.004	.623	.025	0	0
17	20.0	350	0	0	0	1.0	0	0	0
18	20.0	500	0	0	0	1.0	0	0	0
19	20.0	700	0	0	0	.999	.001	0	0
20	20.0	1,000	0	0	0	.999	.001	0	0

TABLE B3-2

$MgSO_3$ DECOMPOSITION WITH CH_4 REDUCTANT

Case	Stoich.	Temp. (°C)	$\Delta H\left(\frac{kcal}{kg}\right)$	Solid (mole fraction)			Gas (mole fraction)				
				MgO	$MgSO_4$	$C_{(gr)}$	CH_4	H_2	H_2O	CO_2	CO
1	.95	350	+ 101	.849	.151	0	0	0	.400	.318	0
2	.95	500	+ 224	1.0	0	0	0	0	.392	.270	0
3	.95	700	+ 319	1.0	0	0	0	.002	.365	.249	.001
4	.95	1,000	+ 421	1.0	0	0	0	.014	.391	.229	.015
5	1.0	350	+ 107	.883	.117	0	0	0	.395	.317	0
6	1.0	500	+ 219	1.0	0	0	0	0	.391	.278	0
7	1.0	700	+ 314	1.0	0	0	0	.002	.366	.256	.001
8	1.0	1,000	+ 419	1.0	0	0	0	.016	.393	.234	.017
9	1.05	350	+ 112	.911	.089	0	0	0	.396	.317	0
10	1.05	500	+ 215	1.0	0	0	0	0	.387	.284	0
11	1.05	700	+ 309	1.0	0	0	0	.002	.365	.263	.001
12	1.05	1,000	+ 417	1.0	0	0	0	.019	.392	.237	.020
13	1.5	350	+ 142	1.0	0	0	0	.001	.226	.330	0
14	1.5	500	+ 188	1.0	0	0	0	.006	.234	.319	.002
15	1.5	700	+ 264	1.0	0	0	0	.032	.263	.278	.022
16	1.5	1,000	+ 428	1.0	0	0	0	.065	.297	.215	.083
17	20.0	350	+ 259	.283	0	.717	.590	.174	.154	.002	0
18	20.0	500	+ 507	.196	0	.804	.393	.408	.116	.008	.006
19	20.0	700	+ 823	.194	0	.806	.299	.519	.057	.004	.059
20	20.0	1,000	+1,432	.137	0	.863	.087	.764	.004	.001	.095

TABLE B3-3

$MgSO_3$ DECOMPOSITION WITH CO REDUCTANT

Case	Stoich.	Temp. (^oC)	(Fraction of total sulfur in each species)						
			S_2	S_8	SO_2	H_2S	COS	CS_2	$MgSO_4$
21	.95	350	.004	.961	.001	-	.001	0	.033
22	.95	500	.271	.607	.075	-	.047	0	0
23	.95	700	.897	0	.071	-	.031	0	0
24	.95	1,000	.837	0	.135	-	.028	0	0
25	1.0	350	.004	.993	.001	-	.002	0	0
26	1.0	500	.277	.612	.038	-	.073	0	0
27	1.0	700	.918	0	.033	-	.048	0	0
28	1.0	1,000	.863	0	.103	-	.034	0	0
29	1.05	350	.004	.896	0	-	.095	.004	0
30	1.05	500	.284	.617	.001	-	.096	.002	0
31	1.05	700	.902	0	.010	-	.087	.002	0
32	1.05	1,000	.883	0	.077	-	.041	0	0
33	1.5	350	.005	.388	0	-	.518	.089	0
34	1.5	500	.069	.001	0	-	.879	.051	0
35	1.5	700	.380	0	0	-	.596	.024	0
36	1.5	1,000	.811	0	.038	-	.150	.002	0
37	20.0	350	.001	0	0	-	.978	.021	0
38	20.0	500	0	0	0	-	.995	.005	0
39	20.0	700	.004	0	0	-	.963	.033	0
40	20.0	1,000	.146	0	0	-	.748	.105	0

TABLE B3-4

$MgSO_3$ DECOMPOSITION WITH CO REDUCTANT

Case	Stoich.	Temp. (^{o}C)		Solid (mole fraction)				Gas $\left(\text{mole fraction}\right)$	
			$\Delta H\left(\frac{kcal}{kg}\right)$	MgO	$MgSO_4$	$MgCO_3$	$C_{(gr)}$	CO_2	CO
21	.95	350	- 386	0	.033	.967	0	.882	0
22	.95	500	- 154	1.0	0	0	0	.847	.001
23	.95	700	- 56	1.0	0	0	0	.768	.005
24	.95	1,000	+ 45	1.0	0	0	0	.705	.058
25	1.0	350	- 396	0	0	1.0	0	.886	0
26	1.0	500	- 169	1.0	0	0	0	.854	.001
27	1.0	700	- 71	1.0	0	0	0	.776	.007
28	1.0	1,000	+ 33	1.0	0	0	0	.708	.068
29	1.05	350	- 398	0	0	1.0	0	.825	.001
30	1.05	500	- 184	1.0	0	0	0	.862	.001
31	1.05	700	- 83	1.0	0	0	0	.773	.013
32	1.05	1,000	+ 24	1.0	0	0	0	.706	.080
33	1.5	350	- 429	.058	0	.779	.163	.679	.002
34	1.5	500	- 235	1.0	0	0	0	.667	.023
35	1.5	700	- 147	1.0	0	0	0	.630	.117
36	1.5	1,000	- 1	1.0	0	0	0	.559	.268
37	20.0	350	- 841	0	0	.051	.949	.949	.002
38	20.0	500	- 729	.055	0	0	.945	.828	.128
39	20.0	700	- 409	.098	0	0	.902	.366	.602
40	20.0	1,000	- 14	1.0	0	0	0	.051	.927

TABLE B3-5

$MgSO_3$ DECOMPOSITION WITH H_2 REDUCTANT

Case	Stoich.	Temp. (^oC)	(Fraction of total sulfur in each species)						
			S_2	S_6	SO_2	H_2S	COS	CS_2	$MgSO_4$
41	.95	350	.004	.152	.002	.607	-	-	.234
42	.95	500	.189	.128	.262	.422	-	-	0
43	.95	700	.393	0	.238	.369	-	-	0
44	.95	1,000	.531	0	.207	.262	-	-	0
45	1.0	350	.004	.150	.002	.634	-	-	.210
46	1.0	500	.189	.117	.232	.463	-	-	0
47	1.0	700	.388	0	.206	.406	-	-	0
48	1.0	1,000	.531	0	.176	.293	-	-	0
49	1.05	350	.004	.147	.002	.661	-	-	.186
50	1.05	500	.187	.104	.203	.506	-	-	0
51	1.05	700	.379	0	.176	.445	-	-	0
52	1.05	1,000	.526	0	.147	.327	-	-	0
53	1.5	350	.001	0	0	.999	-	-	0
54	1.5	500	.004	0	.002	.994	-	-	0
55	1.5	700	.031	0	.011	.958	-	-	0
56	1.5	1,000	.173	0	.047	.779	-	-	0
57	20.0	350	0	0	0	1.0	-	-	0
58	20.0	500	0	0	0	1.0	-	-	0
59	20.0	700	0	0	0	1.0	-	-	0
60	20.0	1,000	0	0	0	1.0	-	-	0

TABLE B3-6

$MgSO_3$ DECOMPOSITION WITH H_2 REDUCTANT

Case	Stoich.	Temp. (°C)	$\Delta H\left(\frac{kcal}{kg}\right)$	Solid (mole fraction)		Gas (mole fraction)	
				MgO	$MgSO_4$	H_2O	H_2
41	.95	350	- 194	.766	.234	.672	0
42	.95	500	- 33	1.0	0	.650	0
43	.95	700	+ 49	1.0	0	.653	.003
44	.95	1,000	+ 162	1.0	0	.668	.022
45	1.0	350	- 202	.790	.210	.675	0
46	1.0	500	- 52	1.0	0	.656	0
47	1.0	700	+ 30	1.0	0	.661	.003
48	1.0	1,000	+ 146	1.0	0	.675	.024
49	1.05	350	- 211	.814	.186	.678	0
50	1.05	500	- 70	1.0	0	.661	0
51	1.05	700	+ 11	1.0	0	.668	.003
52	1.05	1,000	+ 131	1.0	0	.679	.027
53	1.5	350	- 292	1.0	0	.666	0
54	1.5	500	- 237	1.0	0	.664	.004
55	1.5	700	- 154	1.0	0	.653	.021
56	1.5	1,000	+ 10	1.0	0	.608	.101
57	20.0	350	-1,116	1.0	0	.050	.925
58	20.0	500	- 873	1.0	0	.050	.925
59	20.0	700	- 542	1.0	0	.050	.925
60	20.0	1,000	- 28	1.0	0	.050	.925

TABLE B3-7

$MgSO_3$ DECOMPOSITION WITH CO/H_2 (1:1) REDUCTANT

Case	Stoich.	Temp. (°C)	(Fraction of total sulfur in each species)						
			S_2	S_8	SO_2	H_2S	COS	CS_2	$MgSO_4$
61	.95	350	.005	.499	.002	.345	.001	0	.147
62	.95	500	.233	.308	.186	.270	.003	0	0
63	.95	700	.560	0	.182	.250	.007	0	0
64	.95	1,000	.653	0	.178	.158	.010	0	0
65	1.0	350	.006	.510	.002	.362	.001	0	.120
66	1.0	500	.237	.301	.154	.305	.003	0	0
67	1.0	700	.561	0	.149	.282	.008	0	0
68	1.0	1,000	.661	0	.147	.180	.012	0	0
69	1.05	350	.006	.520	.002	.379	.001	0	.092
70	1.05	500	.239	.289	.124	.345	.003	0	0
71	1.05	700	.541	0	.125	.307	.025	0	0
72	1.05	1,000	.631	0	.164	.174	.031	0	0
73	1.5	350	0	0	0	.994	.006	0	0
74	1.5	500	.014	0	0	.940	.046	0	0
75	1.5	700	.121	0	.002	.788	.089	.001	0
76	1.5	1,000	.431	0	.009	.520	.039	.001	0
77	20.0	350	0	0	0	.999	.001	0	0
78	20.0	500	0	0	0	.995	.005	0	0
79	20.0	700	0	0	0	.976	.024	0	0
80	20.0	1,000	.001	0	0	.965	.033	.001	0

TABLE B3-8

$MgSO_3$ DECOMPOSITION WITH CO/H_2 (1:1) REDUCTANT

				Solid (mole fraction)			Gas (mole fraction)				
Case	Stoich.	Temp. (°C)	$\Delta H\left(\frac{kcal}{kg}\right)$	MgO	$MgSO_4$	$C_{(gr)}$	CO_2	CO	H_2O	H_2	CH_4
61	.95	350	- 216	.853	.147	0	.482	0	.308	0	0
62	.95	500	- 103	1.0	0	0	.423	0	.303	0	0
63	.95	700	- 17	1.0	0	0	.398	.001	.295	.001	0
64	.95	1,000	+ 89	1.0	0	0	.366	.025	.317	.012	0
65	1.0	350	- 224	.880	.120	0	.483	0	.308	0	0
66	1.0	500	- 120	1.0	0	0	.432	0	.301	0	0
67	1.0	700	- 35	1.0	0	0	.407	.002	.294	.002	0
68	1.0	1,000	+ 75	1.0	0	0	.371	.028	.318	.013	0
69	1.05	350	- 232	.908	.092	0	.483	0	.309	0	0
70	1.05	500	- 137	1.0	0	0	.440	0	.296	0	0
71	1.05	700	- 50	1.0	0	0	.406	.005	.295	.002	0
72	1.05	1,000	+ 81	1.0	0	0	.322	.073	.327	.013	0
73	1.5	350	- 312	1.0	0	0	.498	0	.168	0	0
74	1.5	500	- 265	1.0	0	0	.481	.003	.184	.002	0
75	1.5	700	- 180	1.0	0	0	.429	.032	.224	.009	0
76	1.5	1,000	- 27	1.0	0	0	.352	.100	.262	.042	0
77	20.0	350	-1,132	.082	0	.918	.247	.001	.501	.052	.153
78	20.0	500	- 983	.089	0	.911	.259	.032	.347	.213	.107
79	20.0	700	- 442	.197	0	.803	.110	.330	.091	.415	.024
80	20.0	1,000	- 16	1.0	0	0	.019	.480	.031	.444	0

The amount of elemental sulfur that can be formed is of interest. For CO at a stoichiometry of 1.0, the amount of gas phase sulfur (S_2 + S_8) is always above 80% with temperature of 400°C and lower yielding 90% elemental sulfur. The other sulfur containing gaseous species are COS and SO_2. The remaining COS, SO_2, and CO are in the proper stoichiometry to yield elemental sulfur.

For H_2 at a stoichiometry of 1.0, the amount of gas phase sulfur and H_2S are considerably less than with CO. Further processing with removal of sulfur and water would be required to shift the equilibrium to favor production of more elemental sulfur.

In the cases where an excess of reducing gas was used all of the excess H_2 tends to go to H_2S and all of the excess CO to COS. The only incentive to run an excess of reducing gas would be for kinetic considerations.

The heat balance numbers are of interest because it will be desirable to eliminate or minimize the transfer or addition of heat. For the inlet conditions chosen (25°C for $MgSO_3$ and CH_4, and 1000°C for CO and H_2) it is seen that methane (see Table B3-2) would require addition of heat even for an outlet temperature of 350°C. The reactor would be endothermic under all conditions investigated and would require addition of heat.

For CO (see Table B3-4) the reactor is exothermic for exit gas and solid temperatures in the range of 700°C and below, and endothermic at 1000°C and above. The adiabatic operating temperature is between 700 and 1000°C.

For H_2 (see Table B3-6) the exothermic operating range is up through 500°C. The endothermic range includes 700°C and above. The adiabatic operating temperature is between 500 and 700°C. Heat requirements for mixtures of H_2 and CO (see Table B3-8) fall between those of the pure components.

The heat balance considerations discussed above are for special cases. They do serve as a guide for considering what type process arrangement is feasible.

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